ION EXCHANGE MEMBRANES

SUMMARY

THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

BY
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SUMMARY

Transport processes occurring across parchment supported and polystyrene based inorganic precipitate membranes have been investigated by taking into the ionic transport, membrane potential, electrical conductivity, ionic distribution equilibria, and spatial distribution of ions and potential within the membrane.

The work described in the thesis has been divided into three parts.

Part I deals with the conductance measurements of parchment supported silver ferrocyanide, manganese ferrocyanide and cobalt ferrocyanide membranes in contact with different concentrations of a number of electrolytes at 10, 15, 20, 25, 30 and 35 ($\pm$ 0.1°C). The conductance data have been used to calculate various thermodynamic parameters like Energy of activation E_a, Free energy of activation $\Delta F^{\#}$, and Entropy of activation $\Delta S^{\#}$ etc. by the application of absolute reaction rate theory. The results of the investigations are that the membrane conductance can be determined at different temperatures with reasonable accuracy. The membranes are weakly charged and ionic species retain

their hydration shell, at least partially, while diffusing through the membrane pores. Negative $\Delta S^{\neq}$ values suggest that the partial immobilization of ion takes place. The immobility of ions within the membrane phase has been ascribed to the interstitial permeation, and the interactions of ions with the fixed charge groups of the membrane skeleton. The interionic distance (or jump distance) for the systems under investigation have been found to be 1.5 A^{0} which is consistent with the empirical values chosen by various investigators.

Part II deals with the characterization and evaluation of effective fixed charge density of polystyrene based stannous ferrocyanide, stannic ferrocyanide, and stannic phosphate membranes in contact with various 1:1 electrolytes at different concentrations from the membrane potential measurements. The Teorell-Meyer and Sievers method; the methods developed by Kobatake and Co-workers; and the most recently developed method of Tasaka et al. based on the principles of irreversible thermodynamics were utilized for the charge density determinations.

The values of effective fixed charge densities evaluated from the different methods were almost the same. The slight deviations has been accounted to the

different procedure adopted for the evaluation. Various theoretical predictions of the Kobatake et. al's theory as well as those of Tasaka et. al's theory were borne out quite satisfactorily by our experimental results. It has, therefore, been concluded that the methods developed recently based on thermodynamics of irreversible processes for the evaluation of effective fixed charge density are valid for the membrane-electrolyte systems under investigation and other such systems.

Part III of the thesis describes the evaluation of selectivity of the parchment supported inorganic precipitate membranes towards simple metal ions from bionic potential and electrical conductance measurements. The selectivity sequence of membranes for cations were as follows:

$$K^+ > Na^+ > Li^+$$

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This is to certify that the thesis entitled "Ion Exchange Chromatography" submitted to the Aligarh Muslim University, Aligarh describes the original work carried out by Dr. Mohd. Iqbal Khan under my supervision and is suitable for the award of Ph. D. degree in Chemistry.

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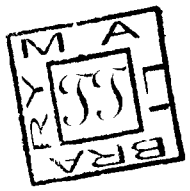

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CONTENTS

GENERAL INTRODUCTION

Transport processes occurring across artificial membranes separating different electrolyte solutions have been one of the most studied electrochemical and bioelectric phenomena. The main objective of the study have been to understand the mechanism of transport so that with the knowledge so gained it would be possible to fabricate membranes of any desired property or properties. Artificial membranes have also been used as models for the physiological membranes in order to understand the behaviour of complex cell membranes in terms of established physicochemical principles. The recent progress pertaining to membrane diffusion and transport problems have been achieved in varying fields like Chemistry, Biochemistry, Physiology, Pharmacology, Biophysics, and Industrial Chemistry etc. in which the starting points and aims have been different. There are several areas of membrane research which have potentially far-reaching consequences to medicine and Chemical industry. Work in this field is contributing significantly to the economic prosperity and physical well being of all mankind.

According to Sollner (1,2) "a membrane is defined as a phase or structure interposed between two

phases or compartments which obstructs or completely prevents gross mass movement between the latter, but permits passage, with various degrees of restriction, of one or several species of particles from the one to the other or between the two adjacent phases or compartments, and which thereby acting as a physicochemical machine transforms with various degrees of efficiency according to its nature and composition of the two adjacent phases or compartments". In simple terms it is described as a phase, usually heterogeneous, acting as a barrier to the flow of molecular and ionic species present in the liquids / or vapors contacting the two surfaces (3). The term heterogeneous has been used to indicate the internal physical structure and external physicochemical performance (1,4-6). From this point of view, most membranes in general, are to be considered heterogeneous, despite the fact that, conventionally, membranes prepared from coherent gels have been homogeneous (7).

Membranes may be solid, liquid, or gas (8) and the outer phases are usually liquid or solid. Although it is frequently the case that membranes are thin in one dimension relative to the other two dimensions. This property is only a functional or operational. In order to achieve a measurable chemical change or

electrochemical effect and to make chemical or electrochemical measurements on a membrane system in a reasonable time, some transport related property must be susceptible to temporal change. Thus, a change in potential, flux, or concentration (among many varying and measurable quantities) require sample thicknesses such that $d^2/2D$ is comparable with the observation time (D is mean diffusion coefficient). Although irregularly shaped membranes are conceivable, most theories and experiments are restricted to systems with one dimensional or spherical symmetry such that transport occurs in one dimension, the X direction in parallel face, planer membranes or along a radius in membranes with spherical shape.

Membranes are considered to be porous or nonporous depending upon the extent of solvent penetration (9). At the nonporous extreme are membranes which are monionic and contain negligible transportable species at equilibrium. Capacion, quartz, anthracene crystals, and teflon films between metal electrodes or electrolyte bathing solutions are solid membrane examples. At the other extreme are porous membranes, which can be saturated and will contain components from the outer phases. Among these are monionic films such as collisphere, inorganic gels and loosely compressed

powders in contact with aqueous solutions. These materials absorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts. Those widely studied are those membranes of polyelectrolytes ("solid" ion exchangers), aqueous - immiscible organic liquid electrolytes ("liquid" ion exchangers) (3,10-12), various permanent supported inorganic precipitates (13-27), solid ion conducting electrolytes including silver halides, rare earth fluorides, and alkali silicate and amino-silicate glasses (28 - 31). All of these materials contain ionic or ionizable groups within the membrane which are capable of transport under diffusive or electric field forces. In addition, these materials possess the properties of porosity. Polyelectrolytes tend to swell rapidly by osmotic pressure driven uptake of solvent. Liquid ion exchangers are surprisingly slow to take up water, while the inorganic salts have no tendency to hydrate. Glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte during uptake of water (32 - 34).

A characteristic of the membrane is the presence of charge sites (10, 35-37). If ionic groups are fixed in membrane as $-SO_3^-$ and COO^- attached to certain exchange resin, the membrane is considered to possess

membranes has been discouraged unless the precise electrostatic connotation is involved (7). It is important to know that cellulose triacetate, which is initially site free, upon develops negative sites by hydrolysis and oxidation on exposure to aqueous solutions.

Membranes may be broadly classified into natural and artificial. Natural membranes are considered to possess a fundamental unit membrane structure which is a bimolecular leaflet of lipid with their polar groups oriented towards the two aqueous phases of the cell, and protein is supposed to exist close to the polar heads of the leaflet. This type of the universal structure is absent in artificial membranes. Lakshminarayanaiah (3) has given a classification of artificial membranes on the basis of its preparation under the headst (A) Operationally useful membranest (i) Homogeneous, and (ii) Heterogeneous membranes which are subdivided into (a) non reinforced membranes, (b) fabric backed or reinforced (c) membranes formed by chemical treatment of other films or membranes, (d) membranes formed by the mechanical treatment of the membrane forming monomers or polymers, and (e) membranes formed by photochemical treatment; (B) Membranes to serve as models for natural membranes; (C) Composite and other special membranes.

A membrane can be categorized according to whether it contains sites for ion exchange or it is site-free, and if it is an ion exchanger, according to whether its sites are fixed or mobile and whether the sites and their counterions are associated or dissociated. This type of classification has been proposed by Sollner, Sandblom and Walker (38). These authors have, however, restricted their discussion to membranes whose properties are considered to be homogeneous in the plane of the membrane, and have avoided explicity with the complexities which result from either mozaic membranes, in which local eddy currents occur, or series membranes, in which space-charge regions exist analogous to those p-n semiconductor junction.

Characterization of membranes in terms of their permeabilities to solvents, solutes, and individual ions is fundamentally important from the very definition of "membrane". Quantitative expression of permeability follows latter. Two general descriptions apply, however. Semipermeability is a measure of preferential solvent transport by a membrane. The reflection coefficient (or rejection coefficient) for solutes, σ is defined according to :

$$1 - \sigma s = t_s / s_o$$

where t_s is transport number (volume fraction) of

solute in the liquid passing through the membrane in a permeation experiment and X_s is the volume fraction of solute in the bathing solution on one side ($X_s = 0$ on the other). When $\sigma - S = 1$, only solvent permeates the membrane (solution is reflected) and the membrane is considerably ideally semipermeable. When the membrane is equally permeable to solute and solvent, $\sigma - S = 0$. Permselectivity is a measure of the current carrying ability of ions in a membrane. Ideal cation permselectivity occurs when the cation transference number $t_c = 1$, i.e. all current is carried through the membrane by cations and $t_a = 0$. The converse definition applies to anion permselectivity. This property is indispensable for the generation of membrane potentials at zero or finite current, and occurs in quasithermodynamic relations between potential and external ion activities.

At one time it was thought that movement of substances through membranes was determined solely by the concentration gradient. This is true in some instances, but movement against a concentration gradient has been observed in some other cases. For example, potassium is usually accumulated in plant and animal cells to a concentration many times that is in the medium surrounding the cells. Such transport requires expenditure of energy by the cells and has been called

active transport or metabolically linked transport, while that which responds to a concentration gradient is passive transport. The term active transport is used in different ways by various authors, no definition being at present satisfactory to every one (39).

While some molecules move directly through pores in the cell membrane for example water molecules and ions of small diameter, there is evidence that other molecules become attached to the carrier with which they form complex in the cell membrane. The complex moves the substance across the membrane liberating it on the other side. Since the carrier which shuttles the molecules from one side of the membrane to the other facilitates diffusion, such movement is spoken of as a facilitated diffusion. Facilitated diffusion can be distinguished from simple diffusion by the kinetics of its entry relative to concentration. The flux through the membrane by simple diffusion increases linearly with increase in concentration of substance, while flux by facilitated diffusion levels with increasing concentration. This is thought to mean that the carrier sites in the membrane become more and more completely occupied until, when additional sites can be occupied, there is no further increase in flux, a phenomena called saturation. Although the carrier complex requires energy of activation to cross the

membrane barrier, less energy is required than for activated diffusion, because of the affinity of the carrier for components (especially lipid) in the membrane. The flux for a given substance is therefore greater when a carrier is involved than in its absence. The kinetics of facilitated diffusion resemble those of active transport.

Not much is known of the mechanism of active transport, but the process seems to be quite general in plant cells, animal cells and microorganisms. Many suggestions for the mechanism of active transport have appeared in the literature, including a working model for ion transport. Summaries of these hypothesis, including figures and references to other literature, are available (Granick and Schwartz (40), Dawson (41) and Giese (39).

At present we are far from a single hypothesis concerning the nature of active transport as we were few years ago, but certain issues have been settled. There seems to be general consensus that a carrier is involved in both facilitated diffusion and active transport and that the carrier is a protein. It has been shown that the carrier protein is not itself an enzyme but is linked to an enzyme or enzymes and the

energy from ATP or some similar high energy phosphate bond is made available for active transport. Although, considerable evidence has accumulated pointing to the sodium pump as the prime mover and suggesting that the movement of other molecules cotransport, as powered, there is contrary evidence that this situation is not general. The problem remains open.

The subject of transport through membranes is a difficult one in which the literature is extensive and frequently not coherent. Many theories on the transport of charged or uncharged particles across membranes have been forwarded. These are roughly divided, according to Schlögl (42 - 44) into three groups:

Groups one considers the membrane as a surface of discontinuity setting up different resistances to the passages of the various molecular or ionic species (45, 46). The driving forces are the differences of the general chemical potential between the two other media. (Differences of pressure or electrical chemical potential). Groups two considers the membrane as a quasihomogeneous intermediate phase of finite thickness in which the local gradients of the general chemical potential act as driving forces (38, 47). Convection may also contribute to particle transport within the

membrane. Group three considers the membrane as a series of potential energy barriers lying one behind the other, thus forming, in contrast to group 2, an inhomogeneous intermediate phase (48 - 50). An (irregular) spatial lattice is formed due to the higher probability of finding a particle in the portions between the activation thresholds. The driving forces arise from the differences between the transition probabilities in opposite directions perpendicular to the membrane.

This grouping attempt to classify the various mathematical approaches, according to the ideal models on which they are based. It is in fact too schematic as many theories occupy intermediate positions. No author is likely to take the view that one of these treatments is right and the other wrong. The various descriptions supplement each other, and depending on the system under consideration, one of the three will prove the most suitable. It may be shown, for example, that when the number of activation thresholds become very large, and the distances between the lattice points sufficiently small, then groups 3 and 2 merge into each other. A transition is also found between groups 1 and 2 (43-44).

Unlike group 3, groups 1 and 2 can be classified in general scheme of irreversible thermodynamics. In group 1 as well as in group 2 , linear relationships are assumed between the particle fluxes and driving forces. Owing to the differing characters of the driving forces, group 1 is treated according to the method of "discontinuous systems", and group 2 according to that of "continuous system". An integration in group 2 across the membrane does not as a rule yield a linear relationship between the flux and the general chemical potential differences. Only for sufficiently small differences does group 2 merge into group 1 after integration. In this sense group 2 is more general than group 1. Group 2 is, however, inferior to group 1 in that a number of idealization can be effected. Kirkwood (51) finds a connection between group 1 and 2. His initial flux equation differs from that normally used in the treatment of "continuous system" in irreversible thermodynamics. This treatment of Kirkwood has been developed and modified by Schlögl. On a broad basis, it may be said that the theories of group 1 are based on the ideals of classical thermodynamics. The theories of group 2, apart from being more rigorous and realistic allow a better description and understanding of transport phenomena in membranes and are useful in

dealing with non-isothermal systems. The theories of group 3 provide a general and unified view applicable to systems of differing degrees of complexity. Many of the theories based on the Nernst Planck flux equation are placed in the first group whereas those dealing with the principles of irreversible thermodynamics and the theory of absolute reaction rates are placed in the 2nd and 3rd groups respectively.

The theories of the first group have the advantage of being relatively simple. For ion-exchange membranes, however they are often inadequate. These theories deal chiefly with processes occurring within the membrane. For such a purpose the theories of the second group are proper choice.

The most important theories of the second group are based either on quasi-thermodynamics or on the thermodynamics of irreversible processes. The fundamental difference between these two approaches are summarized below:

Quasi-thermodynamics is not interested in particle fluxes. One might say that the quasi-thermodynamics approach consists in taking a snapshot of the system and calculating the emf from the changes which a reversible electric current would produce in the

system if it were "frozen" in the state in which the photographic picture was taken. This procedure gives directly the emf of the cell. No model is needed. Taking the snapshot, is often not as simple as it may seem. A rigorous treatment would require the knowledge of the composition of every differential layer of the diffusion zone (i.e. the concentration profiles of all species). Since obtaining this information experimentally is usually too lengthy a task or even quite impossible, the quasithermodynamic treatment is forced to make assumption about the condition of the system.

The thermodynamics of irreversible processes (52) in contrast to quasi-thermodynamics, does not require prior knowledge of the concentration profiles. The set of equations of thermodynamics of irreversible processes interrelates all occurring "fluxes" (electric current, heat etc.) and "driving forces" (gradients of chemical potential, electric potential, temperature etc.). From measurements of a sufficient number of "phenomenological coefficients", all fluxes and forces and hence also the emf can be calculated without the prior knowledge of the profiles and without using the concepts of "reversible energy production" on which quasi-thermodynamics is based. Furthermore, thermodynamics of irreversible process is applicable also to non-

isothermal systems and includes coupling of fluxes which is not covered by quasi-thermodynamics. It may be mentioned here that the discipline of irreversible thermodynamics provides a precise mathematical description of processes of transport and diffusion in membrane systems. Its application to membrane processes is a natural development of the basic theory of Onsager (53) which has been developed by Stavermann (46), Kedem (54), Katchalsky (52), Caplan (55), Meare (56), Spiegler (57, 58), Testagi (59-61), Peterson and Others (62-64) in an extensive and expanding literature.

The theory of absolute reaction rate has also been applied to diffusion processes in membranes by several investigators. Zwolinski, Eyring and Reese (50) presented a detailed kinetic approach to diffusion process which clarifies such established concepts and provide impetus to a fresh approach to the problems in the field of permeability through biological systems and various other membrane systems with varying degrees of complexity. It is equally adaptable to electrolytes, to nonelectrolytes under the driving forces of a concentration potential gradients. Laidler and Shuler (49) have also treated the kinetics of membrane transport under steady state conditions. They employ similar principles

and express the rate constant of the overall process of surface penetration in terms of a number of specific rate constants. Various special cases are considered and discussed with reference to the experimental data. Recently, Tien and Ting (63) have applied the theory of absolute reaction rates to diffusion processes through bilayer lipid membrane (BLM) and have derived various thermodynamic quantities like free energy of activation enthalpy of activation, and entropy of activation etc. These thermodynamic parameters have been utilized to predict the mechanisms of ion transport through living systems.

Application of electrochemistry to the membrane phenomena, according to Buck (7), is pertinent at three levels. One is the development of techniques with application to experimental phenomenology including current-voltage-time-concentration behaviour. A second is the mathematical modeling implied by experiment and tested against experiment. The third level is the experimental verification of models in terms of the molecular determination of theoretical parameters by electrical methods and by complementary nonelectrochemical methods, physical, optical, esr, nmr, Raman fluorescence, T-jump techniques etc. From transient and steady state measurement of current or membrane potential as a func-

tion of chemical composition, chemical treatment, and temperature, the roles of kinetic and equilibrium parameters can be deduced or inferred. A possible approach to modeling begins with the assumption of the membrane as a linear system to which laws of network theory may be applied. Another begins by solution of basic electrodiffusion laws of transport with equilibrium or kinetic boundary conditions in order to deduce forms for system functions which satisfy the data.

The solution to a problem in science is often achieved by slow and laborious collection of data. Pertinent observations are made and data already available are focussed on the problem in question and a possible explanation, a hypothesis, is formulated. Carefully planned experiments are then prepared for testing it may happen that after much work an investigator finds that the attempted explanation is inadequate and that he has only cleared the ground for further analytical work. An alternative hypothesis is then constructed and tested. Occasionally decisive experiments result in dramatic advances in knowledge and understanding. Such decisive experiments have occurred more frequently in physics and chemistry, in which total number of variables are fewer. In the biological system, in which there are great number of variables, similar progress in theoretical knowledge is quite slow and may be expected only

as the physiologist gain control on these factors.

In this thesis studies of transport properties of polystyrene based and parchment supported inorganic precipitate membranes when they are used to separate various aqueous electrolyte solutions are reported. The choice of the systems are based on the findings of Teorell (35,37) that parchment in some formal aspect behave like gastric mucosal membrane and that the composite membranes mimic some of the properties of biological cells. The findings of Teorell that the electrolytic transport processes in stomach could be handled by something similar to Fick's diffusion law and that Nernst-Planck formula for electrical potential were applicable, has encouraged us to proceed further with the studies of the electrochemical properties of artificial membranes (both parchment supported and polystyrene based) as models for biological systems.

The membrane-electrolyte system, in our study, has been considered to contain four chemical species, 1) Counterion, 2) Coion, 3) Water and fourth the membrane matrix which carried fixed ionogenic groups and excludes the possibility of chemical reaction within the membrane. The membrane matrix has, therefore, been considered to consist of fixed charge and adjacent

polymer segments which together constitute the repeat unit of matrix. It is, therefore, possible that kinetic coupling interaction of membrane matrix will include not only the contribution of fixed charge, but also specific polymer effects if such exist. This is an important qualification of the species four as simply as ion, although it appears from earlier studies that such effects are small.

The discussion has mainly been restricted to commenting on only a few points concerning the following ionic processes in the membrane system, "Permeability phenomena": (i) membrane potential, (ii) electrical conductivity, (iii) ionic transport "flux", (iv) ionic distribution equilibria, (v) spatial distribution of ions and the potential within the membrane.

The thesis has been presented under the following heads:

(1) <u>Membrane Conductance and Application of Absolute Reaction Rate Theory:</u>

This portion describes the measurements of conductance of membranes in contact with different concentrations of uni-univalent, bivalent and trivalent

electrolytes at 10, 15, 20, 25, 30 and 35 (± 0.1 °C). The data have been used to calculate various thermodynamic parameters like Energy of activation E_a, Enthalpy of activation $\Delta H^{\neq}$, Free energy of activation $\Delta F^{\neq}$, Entropy of activation $\Delta S^{\neq}$ by the application of absolute reaction rate theory.

(2) <u>Membrane Potential and Evaluation of Charge Density:</u>

This portion deals with the measurements of membrane potential across polystyrene based inorganic precipitate membranes in contact with various 1:1 electrolytes at different concentrations and under isothermal condition for the evaluation of the thermodynamically effective fixed charge density of the membranes. The membrane potential data have also been utilized to examine the validity of the recently developed theoretical equations for membrane potential including those based on the thermodynamics of irreversible processes.

(3) <u>Bionic Potential, Electrical Conductivity and Recently Developed Theories:</u>

This portion deals with the evaluation of

selectivity of parchment supported inorganic precipitate membranes towards simple metal ions from bionic potential and electrical conductance measurements using different 1:1 electrolytes.

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CHAPTER-I

Membrane Conductance and Application of Absolute Reaction Rate Theory:

Ion permeation in membranes is usually characterized by such measurable parameters as Conductance, Current-voltage relationship, ionic flux and membrane potentials. The membrane conductance has been found to dependant on the intrinsic properties such as the fixed Charge Concentration, temperature and composition of the external solutions. The specific conductance of the membrane can be quantitatively predicted from the fixed charge theory of Teorell (1). Two limiting forms for specific conductance of the pore liquid, one in dilute concentration limit and the other in high concentration range have also been found to be related to the fixed charge and the mobility of ions. At very low external concentrations, as found by some investigators (2-5), the specific conductance of the pore solution to exceed that of the external solution. The swelling or rather the deswelling of the membrane with increase in external concentration has been considered in great detail by Mills and Couchore (6,7). The changes in conductance of a polyethylene phosphonate membrane following changes in pH of the external solution have been described by de Mayeny and Couchoux (8-10).

The temperature coefficient of conductance was found to be of the same order as that observed in aqueous solution i.e. about 2% per degree. The activation energy of the conductance depending on the system used, lie between 2 and 6 Kcal/mole (11-14).

For some membranes, particularly of biological origin, the special distribution of the interstitial ionic solution is disturbed in an uneven manner on application of current used for measurement of membrane resistance. This gives rise to non linear resistances. In such cases, one measures the theoretical resistance per unit area as

$$R = \frac{1}{F^2} \int_1^{11} \frac{dx}{U+V} \qquad (1.1)$$

where $U = \Sigma \bar{u}_i \Gamma_i$ for cations and $V = \Sigma \bar{v}_i \Gamma_i$ for anions. As a result, the non linear character of the membrane resistance is considered in terms of the concepts of dynamic resistance (15) which is defined as dE / di. Explicit expressions for the special cases have been given by Teorell. For the total conductance G of a biological membrane, Hodgkin and Katz derived

$$G = \frac{F^2}{(RT)^2} \Delta E \bar{P}_K \frac{[K]_o}{[Na]_i} \qquad (1.2)$$

where i and R are expressed in terms of $\bar{U}$ and $\bar{V}$ and

$$P_K = RT\,\bar{u}_K / d$$

The expression for partial conductance i.e. a fraction of G due to any one ionic species, at equilibrium has been obtained by Hodgkin and Lindesheim (16). The Nernst Flux equation has been used to derive the expression for the total conductance i.e.

$$G = \frac{F^2}{RT} \sum_i z_i^2 J_i \qquad (1.3)$$

Recently Kobatake and Tasaki (17) have integrated eq. 1.1 for the simplest case of two univalent cations and obtained the relation

$$\gamma J_i = RT / F^2 \qquad (1.4)$$

These authors found that this expression followed the artificial membranes as well as biological membranes (squid axonal membranes) both in their resting and active states.

The absolute reaction rate theory (18) has been applied to diffusion processes in membranes by several investigators. Rosinski, Eyring and Reese (19) considered the diffusion processes as one of the basic phenomena for sustaining the growth and development of plants and organism. They presented a detailed kinetic

approach to diffusion which clarifies much established concepts and provide impetus to a fresh approach to the problems in the field of biological diffusion. Shuler, Dumas and Laidler (20) have also treated the kinetics of membrane transport under steady state conditions. Tien and Ting (21) have applied the theory of absolute reaction rates to diffusion processes through Bilayer Lipid Membranes (BLM) for the investigation of actual mechanism of transport through living systems. Recently, Teorell and Petropoulos (22) determined the diffusion coefficient of alkali-metal ion through cellulose acetate membrane and discussed in terms of porous structure model; and Iijima and Co-workers (23) through polyamide membrane used activation analysis for the investigation of the mechanism of the diffusion of ions of simple salts. Many workers and various theories on the diffusion of simple salts in membranes have been reported and are reviewed comprehensively by Helffrich (24,25), Lakshminarayanaiah (26), Sack (27) and Others in an expanding literature.

In this chapter, the conductance measurements of parchment supported silver ferrocyanide, manganese ferrocyanide and Cobalt ferrocyanide membrane in contact with different concentrations of uni-univalent,

bivalent and trivalent electrolytes at 10, 15, 20, 25, 30 and 35 ($\pm$ 0.1 ^{0}C) are described. The conductance data have been used to calculate various thermodynamic parameters like Energy of activation E_a, Enthalpy of activation $\Delta H^{\neq}$, Free energy of activation $\Delta F^{\neq}$, Entropy of activation $\Delta S^{\neq}$ by the application of absolute reaction rate theory.

EXPERIMENTAL PROCEDURE

Parchment supported Silver, manganese and Cobalt ferrocyanide membranes were prepared by the method of interaction suggested by Sag and Co-workers (28-30). Parchment paper (supplied by M/s. Baird and Tatlock Ltd. London) was soaked in distilled water and tied to the flat bottom of a glass tube. A 0.01 M solution of potassium ferrocyanide was taken inside it. The tubes were then suspended in the solutions of 0.01 M silver, manganese and cobalt chloride for about 72 hr. The two solutions were interchanged latter and kept for another 72 hr. The membranes, thus obtained, were washed with deionized water for the removal of free electrolytes. It was then cut into a circular disc form and sealed between two half cells of an electrochemical cell of the type shown in Fig. 1 . The half cells were first filled with electrolyte solutions to equilibrate the membranes. The solutions were then replaced by purified mercury without removing the adhering surface liquid (31). Platinum electrodes dipping in mercury were used to establish electrical contact. The membrane conductance was monitored on a Digest Reading Conductivity Meter 305 (Systronic) at a frequency of 10^3 Cps. All

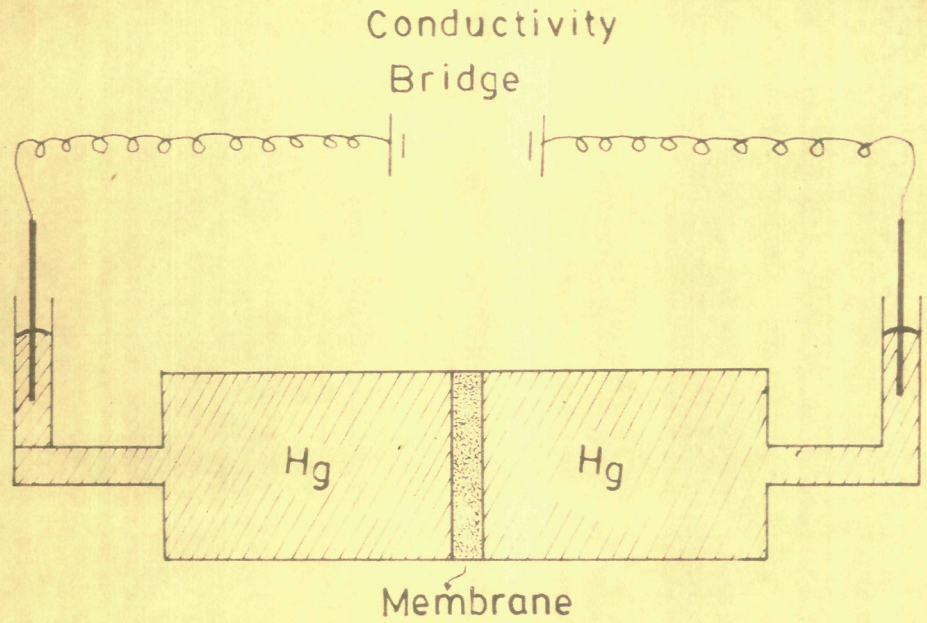

Fig.1.1: Cell for measuring electrical conductivity

measurements were carried out using a water thermostat maintained at temperatures 10, 15, 20, 25, 30 and 35 (± 0.1 °C). The electrolyte solutions were prepared from analytical grade reagents and deionized water.

Extensive use of the method has indicated that, to realize reproducible results there should be no trapped air particularly at the membrane-mercury interface and the mercury used should be purified as it gets easily oxidized.

RESULTS AND DISCUSSION

The conductance of parchment supported silver ferrocyanide , manganese ferrocyanide and cobalt ferrocyanide membranes in contact with various 1:1, 2:1 and 3:1 electrolyte solutions at temperature range 10 to 35 ^{o}C ($\pm$0.1) are given in Tables 1.1 - 1.21 and results are shown in Fig. 1.2 (a, b and c).

The membrane conductance increases almost linearly with the square root of the concentration of the bathing electrolyte solutions and attains a maximum limiting value. This behaviour was seen with all the three membranes in contact with various electrolytes used and at every temperature.

The flow of ion and water are generally larger in more open structure of the membrane and decreases as the membrane shrinks in more concentrated solution in part at least due to the increased obstruction of the polymer matrix as diffusional pathways become more tortuous and the fractional pore volume decreases. On the other hand, the electrical conductivity should increase with the increased salt uptake. These two opposing effects operate simultaneously, and at higher

TABLE 1.1

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS SILVER FERROCYANIDE MEMBRANE FOR KCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES.

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.10×10^{-1}	0.06×10^{-2}	0.06×10^{-2}	0.03×10^{-2}
15°C	0.02×10^{-1}	0.10×10^{-2}	0.07×10^{-2}	0.05×10^{-2}
20°C	0.03×10^{-1}	0.13×10^{-2}	0.10×10^{-2}	0.06×10^{-2}
25°C	0.04×10^{-1}	0.16×10^{-2}	0.12×10^{-2}	0.08×10^{-2}
30°C	0.05×10^{-1}	0.20×10^{-2}	0.15×10^{-2}	0.10×10^{-2}
35°C	0.06×10^{-1}	0.25×10^{-2}	0.19×10^{2}	0.12×10^{-2}

TABLE 1.2

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS MANGANESE FERROCYANIDE MEMBRANE FOR KCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES.

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.04×10^{-1}	0.08×10^{-2}	0.04×10^{-2}	0.03×10^{-2}
15°C	0.05×10^{-1}	0.11×10^{-2}	0.06×10^{-2}	0.04×10^{-2}
20°C	0.06×10^{-1}	0.13×10^{-2}	0.07×10^{-2}	0.05×10^{-2}
25°C	0.07×10^{-1}	0.15×10^{-2}	0.09×10^{-2}	0.06×10^{-2}
30°C	0.08×10^{-1}	0.18×10^{-2}	0.10×10^{-2}	0.07×10^{-2}
35°C	0.09×10^{-1}	0.25×10^{-2}	0.13×10^{-2}	0.08×10^{-2}

TABLE 1.3

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS COBALT FERROCYANIDE MEMBRANE FOR KCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES.

Concentration (mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.08×10^{-1}	0.16×10^{-2}	0.09×10^{-2}	0.03×10^{-2}
15°C	0.10×10^{-1}	0.20×10^{-2}	0.07×10^{-2}	0.05×10^{-2}
20°C	0.12×10^{-1}	0.26×10^{-2}	0.00×10^{-2}	0.06×10^{-2}
25°C	0.14×10^{-1}	0.32×10^{-2}	0.11×10^{-2}	0.08×10^{-2}
30°C	0.17×10^{-1}	0.40×10^{-2}	0.14×10^{-2}	0.09×10^{-2}
35°C	0.20×10^{-1}	0.46×10^{-2}	0.10×10^{-2}	0.12×10^{-2}

TABLE 1.4

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS SILVER FERROCYANIDE MEMBRANE FOR NaCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.04×10^{-1}	0.10×10^{-2}	0.03×10^{-2}	0.01×10^{-2}
15°C	0.06×10^{-1}	0.12×10^{-2}	0.04×10^{-2}	0.02×10^{-2}
20°C	0.08×10^{-1}	0.16×10^{-2}	0.06×10^{-2}	0.03×10^{-2}
25°C	0.07×10^{-1}	0.22×10^{-2}	0.08×10^{-2}	0.05×10^{-2}
30°C	0.09×10^{-1}	0.27×10^{-2}	0.10×10^{-2}	0.06×10^{-2}
35°C	0.11×10^{-1}	0.32×10^{-2}	0.12×10^{-2}	0.07×10^{-2}

TABLE 1.5

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS MANGANESE FERROCYANIDE MEMBRANE FOR NaCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (mol/l) Temperature	0.1	0.01	0.001	0.001
10°C	0.02×10^{-1}	0.07×10^{-2}	0.03×10^{-2}	0.01×10^{-2}
15°C	0.04×10^{-1}	0.10×10^{-2}	0.04×10^{-2}	0.02×10^{-2}
20°C	0.05×10^{-1}	0.13×10^{-2}	0.05×10^{-2}	0.04×10^{-2}
25°C	0.06×10^{-1}	0.15×10^{-2}	0.06×10^{-2}	0.05×10^{-2}
30°C	0.08×10^{-1}	0.18×10^{-2}	0.07×10^{-2}	0.06×10^{-2}
35°C	0.09×10^{-1}	0.21×10^{-2}	0.08×10^{-2}	0.07×10^{-2}

TABLE 1.6

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS COBALT FERROCYANIDE MEMBRANE FOR NaCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	[illegible]	[illegible]	0.04×10^{-2}	0.02×10^{-2}
15°C	[illegible]	[illegible]	0.10×10^{-2}	0.03×10^{-2}
20°C	[illegible]	[illegible]	0.18×10^{-2}	0.07×10^{-2}
25°C	[illegible]	[illegible]	0.30×10^{-2}	0.09×10^{-2}
30°C	[illegible]	[illegible]	0.28×10^{-2}	0.12×10^{-2}
35°C	[illegible]	[illegible]	[illegible]	0.19×10^{-2}

TABLE 1.7

OBSERVED VALUES OF MEMBRANE CONDUCTANCE $X10^2$(MHOS) ACROSS SILVER FERROCYANIDE MEMBRANE FOR LiCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.16	0.05	0.03	0.02
15°C	0.25	0.07	0.04	0.03
20°C	0.30	0.09	0.06	0.04
25°C	0.35	0.12	0.07	0.05
30°C	0.42	0.14	0.08	0.06
35°C	0.55	0.16	0.10	0.08

TABLE 1.8

OBSERVED VALUES OF MEMBRANE CONDUCTANCE $X10^2$(MHOS) ACROSS MANGANESE FERROCYANIDE MEMBRANE FOR LiCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.13	0.04	0.02	0.01
15°C	0.26	0.06	0.03	0.02
20°C	0.30	0.08	0.04	0.03
25°C	0.34	0.10	0.06	0.04
30°C	0.38	0.13	0.07	0.05
35°C	0.43	0.14	0.08	0.06

TABLE 1.9

OBSERVED VALUES OF MEMBRANE CONDUCTANCE $X10^2$(MHOS) ACROSS COBALT FERROCYANIDE MEMBRANE FOR LiCl AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.46	0.10	0.07	0.05
15°C	0.58	0.15	0.09	0.07
20°C	0.70	0.18	0.12	0.09
25°C	0.85	0.20	0.15	0.10
30°C	0.95	0.27	0.20	0.13
35°C	1.00	0.32	0.24	0.15

TABLE 1.10

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS SILVER FERROCYANIDE MEMBRANE FOR $BaCl_2$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.02×10^{-1}	0.04×10^{-2}	0.02×10^{-2}	0.01×10^{-2}
15°C	0.03×10^{-1}	0.07×10^{-2}	0.03×10^{-2}	0.02×10^{-2}
20°C	0.04×10^{-1}	0.10×10^{-2}	0.05×10^{-2}	0.03×10^{-2}
25°C	0.06×10^{-1}	0.13×10^{-2}	0.06×10^{-2}	0.04×10^{-2}
30°C	0.08×10^{-1}	0.17×10^{-2}	0.08×10^{-2}	0.05×10^{-2}
35°C	0.09×10^{-1}	0.21×10^{-2}	0.09×10^{-2}	0.07×10^{-2}

TABLE 1.11

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS MANGANESE FERROCYANIDE MEMBRANE FOR $SmCl_3$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.02×10^{-1}	0.05×10^{-2}	0.01×10^{-2}	0.01×10^{-2}
15°C	0.02×10^{-1}	0.07×10^{-2}	0.02×10^{-2}	0.01×10^{-2}
20°C	0.03×10^{-1}	0.08×10^{-2}	0.03×10^{-2}	0.02×10^{-2}
25°C	illegible	0.10×10^{-2}	0.04×10^{-2}	0.03×10^{-2}
30°C	0.00×10^{-1}	0.12×10^{-2}	0.05×10^{-2}	0.04×10^{-2}
35°C	0.07×10^{-1}	0.14×10^{-2}	0.06×10^{-2}	0.05×10^{-2}

TABLE 1.12

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS COBALT FERROCYANIDE MEMBRANE FOR $SmCl_3$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
illegible	0.08×10^{-1}	0.10×10^{-2}	0.06×10^{-2}	0.02×10^{-2}
illegible	0.07×10^{-1}	0.15×10^{-2}	0.07×10^{-2}	0.04×10^{-2}
illegible	0.14×10^{-1}	0.23×10^{-2}	0.09×10^{-2}	0.06×10^{-2}
illegible	0.17×10^{-1}	0.20×10^{-2}	0.10×10^{-2}	0.09×10^{-2}
illegible	0.20×10^{-1}	0.35×10^{-2}	0.12×10^{-2}	0.12×10^{-2}
illegible	0.23×10^{-1}	0.43×10^{-2}	0.14×10^{-2}	0.16×10^{-2}

TABLE 1.13

OBSERVED VALUES OF MEMBRANE CONDUCTANCE $X10^2$(MHOS) ACROSS SILVER FERROCYANIDE MEMBRANE FOR $CaCl_2$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.15	0.04	0.02	0.01
15°C	0.20	0.06	0.04	0.02
20°C	0.30	0.07	0.05	0.03
25°C	0.40	0.09	0.07	0.05
30°C	0.55	0.10	0.00	0.06
35°C	0.60	0.14	0.10	0.00

TABLE 1.14

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS MANGANESE FERROCYANIDE MEMBRANE FOR $CaCl_2$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.01×10^{-1}	0.02×10^{-2}	0.01×10^{-2}	0.01×10^{-2}
15°C	0.02×10^{-1}	0.04×10^{-2}	0.02×10^{-2}	0.01×10^{-2}
20°C	0.03×10^{-1}	0.06×10^{-2}	0.03×10^{-2}	0.02×10^{-2}
25°C	0.04×10^{-1}	0.06×10^{-2}	0.04×10^{-2}	0.03×10^{-2}
30°C	0.05×10^{-1}	0.08×10^{-2}	0.06×10^{-2}	0.04×10^{-2}
35°C	0.06×10^{-1}	0.10×10^{-2}	0.08×10^{-2}	0.05×10^{-2}

TABLE 1.15

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS COBALT FERROCYANIDE MEMBRANE FOR $CaCl_2$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) / Temperature	0.1	0.01	0.001	0.0001
10°C	0.02×10^{-1}	0.06×10^{-2}	0.04×10^{-2}	0.02×10^{-2}
15°C	0.03×10^{-1}	0.10×10^{-2}	0.06×10^{-2}	0.04×10^{-2}
20°C	0.05×10^{-1}	0.14×10^{-2}	0.08×10^{-2}	0.06×10^{-2}
25°C	0.07×10^{-1}	0.19×10^{-2}	0.09×10^{-2}	0.07×10^{-2}
30°C	0.08×10^{-1}	0.23×10^{-2}	0.12×10^{-2}	0.08×10^{-2}
35°C	0.09×10^{-1}	0.28×10^{-2}	0.15×10^{-2}	0.10×10^{-2}

TABLE 1.16

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS SILVER FERROCYANIDE MEMBRANE FOR $MgCl_2$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) / Temperature	0.1	0.01	0.001	0.0001
10°C	0.13×10^{-2}	0.03×10^{-2}	0.02×10^{-2}	0.16×10^{-3}
15°C	0.16×10^{-2}	0.04×10^{-2}	0.03×10^{-2}	0.22×10^{-3}
20°C	0.19×10^{-2}	0.06×10^{-2}	0.04×10^{-2}	0.28×10^{-3}
25°C	0.22×10^{-2}	0.07×10^{-2}	0.05×10^{-2}	0.30×10^{-3}
30°C	0.24×10^{-2}	0.09×10^{-2}	0.07×10^{-2}	0.44×10^{-3}
35°C	0.26×10^{-2}	0.10×10^{-2}	0.08×10^{-2}	0.53×10^{-3}

TABLE 1.17

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS MANGANESE FERROCYANIDE MEMBRANE FOR $MgCl_2$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.01×10^{-1}	0.02×10^{-2}	0.01×10^{-2}	0.09×10^{-3}
15°C	0.03×10^{-1}	0.03×10^{-2}	0.02×10^{-2}	0.10×10^{-3}
20°C	0.04×10^{-1}	0.04×10^{-2}	0.03×10^{-2}	0.16×10^{-3}
25°C	0.06×10^{-1}	0.05×10^{-2}	0.04×10^{-2}	0.20×10^{-3}
30°C	0.08×10^{-1}	0.07×10^{-2}	0.05×10^{-2}	0.25×10^{-3}
35°C	0.10×10^{-1}	0.09×10^{-2}	0.06×10^{-2}	0.30×10^{-3}

TABLE 1.18

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS COBALT FERROCYANIDE MEMBRANE FOR $MgCl_2$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.001
10°C	0.05×10^{-1}	0.10×10^{-2}	0.03×10^{-2}	0.20×10^{-3}
15°C	0.07×10^{-1}	0.20×10^{-2}	0.06×10^{-2}	0.34×10^{-3}
20°C	0.09×10^{-1}	0.23×10^{-2}	0.08×10^{-2}	0.41×10^{-3}
25°C	0.12×10^{-1}	0.30×10^{-2}	0.10×10^{-2}	0.50×10^{-3}
30°C	0.13×10^{-1}	0.35×10^{-2}	0.13×10^{-2}	0.77×10^{-3}
35°C	0.16×10^{-1}	0.40×10^{-2}	0.16×10^{-2}	0.98×10^{-3}

TABLE 1.19

OBSERVED VALUES OF MEMBRANE CONDUCTANCE $X10^2$(MHOS) ACROSS SILVER FERROCYANIDE MEMBRANE FOR $AlCl_3$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.04	0.03	0.02	0.01
15°C	0.09	0.06	0.04	0.03
20°C	0.14	0.08	0.06	0.05
25°C	0.17	0.11	0.07	0.06
30°C	0.20	0.13	0.09	0.07
35°C	0.25	0.16	0.10	0.09

TABLE 1.20

OBSERVED VALUES OF MEMBRANE CONDUCTANCE $X10^2$(MHOS) ACROSS MANGANESE FERROCYANIDE MEMBRANE FOR $AlCl_3$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.20	0.07	0.03	0.02
15°C	0.29	0.10	0.05	0.03
20°C	0.35	0.12	0.07	0.05
25°C	0.41	0.15	0.08	0.07
30°C	0.46	0.17	0.10	0.08
35°C	0.55	0.19	0.13	0.10

TABLE 1.21

OBSERVED VALUES OF MEMBRANE CONDUCTANCE (MHOS) ACROSS COBALT FERROCYANIDE MEMBRANE FOR $AlCl_3$ AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concentration (Mol/l) Temperature	0.1	0.01	0.001	0.0001
10°C	0.14×10^{-1}	0.06×10^{-1}	0.30×10^{-2}	0.10×10^{-2}
15°C	0.17×10^{-1}	0.00×10^{-1}	0.30×10^{-2}	0.10×10^{-2}
20°C	0.19×10^{-1}	0.11×10^{-1}	0.44×10^{-2}	0.25×10^{-2}
25°C	0.23×10^{-1}	0.13×10^{-1}	0.52×10^{-2}	0.34×10^{-2}
30°C	0.20×10^{-1}	0.15×10^{-1}	0.59×10^{-2}	0.43×10^{-2}
35°C	0.32×10^{-1}	0.17×10^{-1}	0.65×10^{-2}	0.54×10^{-2}

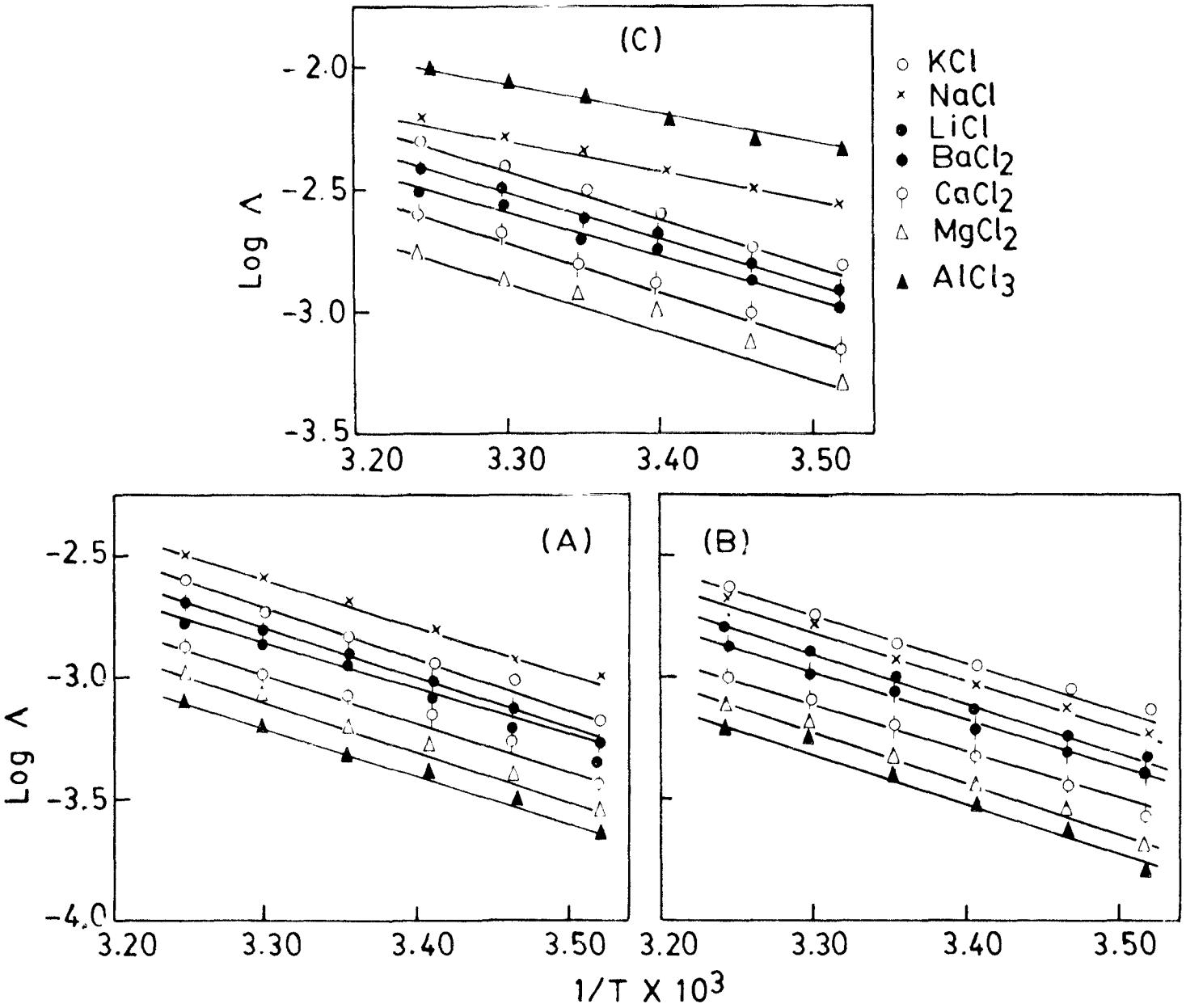

Fig.1.2: Plots of log Λ vs 1/T X 10^3 for various 1:1, 2:1 and 3:1 electrolytes at 0·01 M concentration across (A) Silver ferrocyanide, (B) Manganese ferrocyanide and (C) Cobalt ferrocyanide membranes.

concentration as shown in Fig. 1.3 (a, b and c); the effect of salt uptake by the membrane overcomes the effect of increased tortuosity and thus membrane conductance increases and becomes almost constant. This is in accordance with the findings of Peterson in the case of C 60N and C 60E membranes with NaCl used as invading electrolyte as well as Iijima et. al. (23) for Nylon membranes in contact with various alkali chlorides. The sequence of membrane conductance for alkali-metal ions under the same condition (0.01N, 25 °C) was

$$K^+ > Na^+ > Li^+$$

which is parallel to mobility of alkali-metal ions in aqueous solution. This sequence refers to the fact that the membrane is weakly charged and the ionic species retain their hydration shells at least partially. This is in full agreement with the results of charge density (charge density $\simeq 10^2$ meq/l) of inorganic precipitate membrane and the selectivity sequence of alkali-metal ions in ion exchange resins presented by Helfenberg (32).

Membrane porosity in relation to the size of the species (hydrated) flowing through the membrane seems to determine the above sequence. Although the sizes

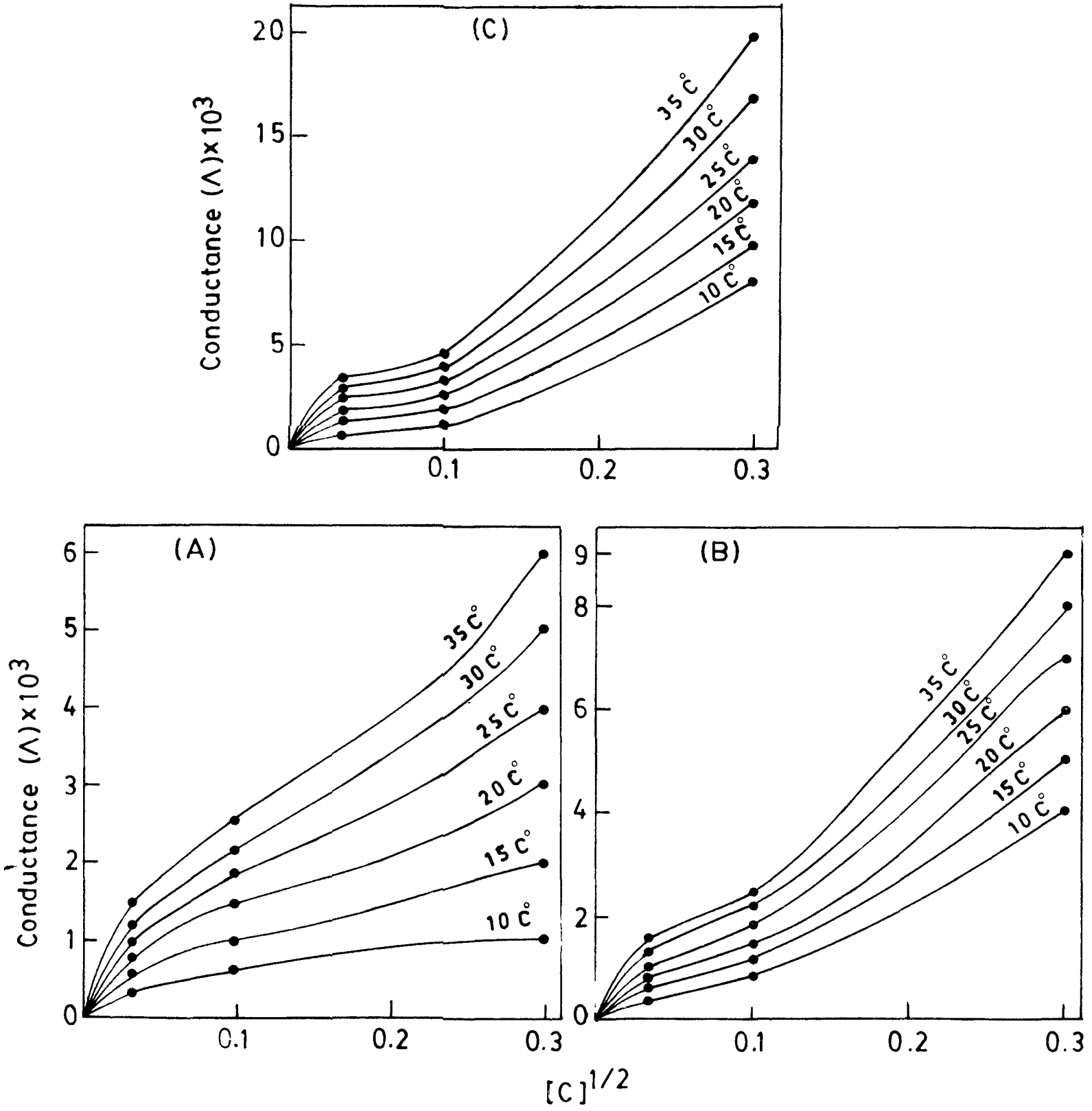

Fig.1·3: Plots of conductance (Λ) $\times 10^3$ against square root of concentration for KCl at different temperature across (A) Silver ferrocyanide, (B) Manganese ferrocyanide and (C) Cobalt ferrocyanide membranes.

of the hydrated electrolytes are not known with certainty, there are few tabulations (33, 34) of the number of water associated with some electrolyte. However a plot of conductance of different electrolytes (chlorides) against free energy of hydration of cation (35) is given for the membranes. It is seen that conductance decreases with increasing hydration energy, that is, greater size due to increase in hydration. This points to the fact that the electrolyte is diffusing along the pores or channels of dimensions adequate enough to allow the substance to penetrate the membrane. The state of hydration of the penetrating electrolyte may be considered to exist in a dynamic condition so that at higher temperatures considerably higher fraction of the total number of a given kind would possess excess energy ΔE according to Boltzmann distribution $f = e^{-\Delta E/RT}$ (R is the gas constant). Under these circumstances, those ionic species which have lost sufficient water of hydration to be smaller than the size of the pore would enter the membrane. This way the conductance would increase with increase in temperature, subject to the proviso that the membrane has undergone no irreversible change in its structure. That no such structural change is involved is evident from the linear plots of $\log \Lambda$ versus $1/T$ shown in Fig. 1.2. The slope of which can

used to give the energy of activation employing Arrhenius equation. The values of energy of activation derived, in this way, are given in Tables 1.22 - 1.42. The activation energy decreases with the increase in concentration of the bathing electrolyte solutions. Comparison of activation energies at 0.01 M leads to the sequence

$$E_{a_{Li^+}} < E_{a_{Na^+}} < E_{a_{K^+}}$$

The activation energies for electrolytic conduction follow the sequence of crystallographic radii of the alkali metal cations. When the penetrant moves in a polymer substrate containing relatively small amount of water, its motion may be governed by the segmental mobility of the polymer and its diffusivity may depend on the probability that the segment will make a hole large enough to accommodate a penetrant species (36). In such a system the activation energy will depend on the size of the penetrant species, that is, the activation energy will increase with the penetrant size. If this is the case in our system, the dependence of the activation energy on the kind of alkali metal ion may be interpreted in terms of the ion's crystallographic radius.

The theory of absolute reaction rates (18) has been applied to diffusion processes in membranes by several investigators (19-21, 37, 38). Following Eyring (18,19) we have

$$\Lambda = \frac{RT}{Nh} e^{-\Delta H^{\neq}/RT} e^{-\Delta S^{\neq}/R} \qquad (1.5)$$

where Λ is the membrane conductance, h is the Planck constant, R is the gas constant, N is the Avogadro's number and T is the absolute temperature. $\Delta F^{\neq}$ is the free energy of activation for the diffusion of ions and is related by Gibbs-Helmholtz equation:

$$\Delta F^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} \qquad (1.6)$$

$\Delta H^{\neq}$ is related to Arrhenius energy of activation Ea by

$$Ea = \Delta H^{\neq} + RT \qquad (1.7)$$

A plot of $\log \Lambda Nh / RT$ Vs. $1/T$ (Fig. 1.4) gives the value of $\Delta H^{\neq}$ and the intercept gives the value of $\Delta S^{\neq}$. The derived values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ may be used to get the value of $\Delta F^{\neq}$ and Ea using eqs. 1.6 and 1.7.

On the other hand, we have Arrhenius type equation.

$$\Lambda = \Lambda_0 e^{-Ea/RT} \qquad (1.8)$$

and

$$\Lambda_0 = 2.72 (KTd^2/h) e^{-\Delta S^{\neq}/R} \qquad (1.9)$$

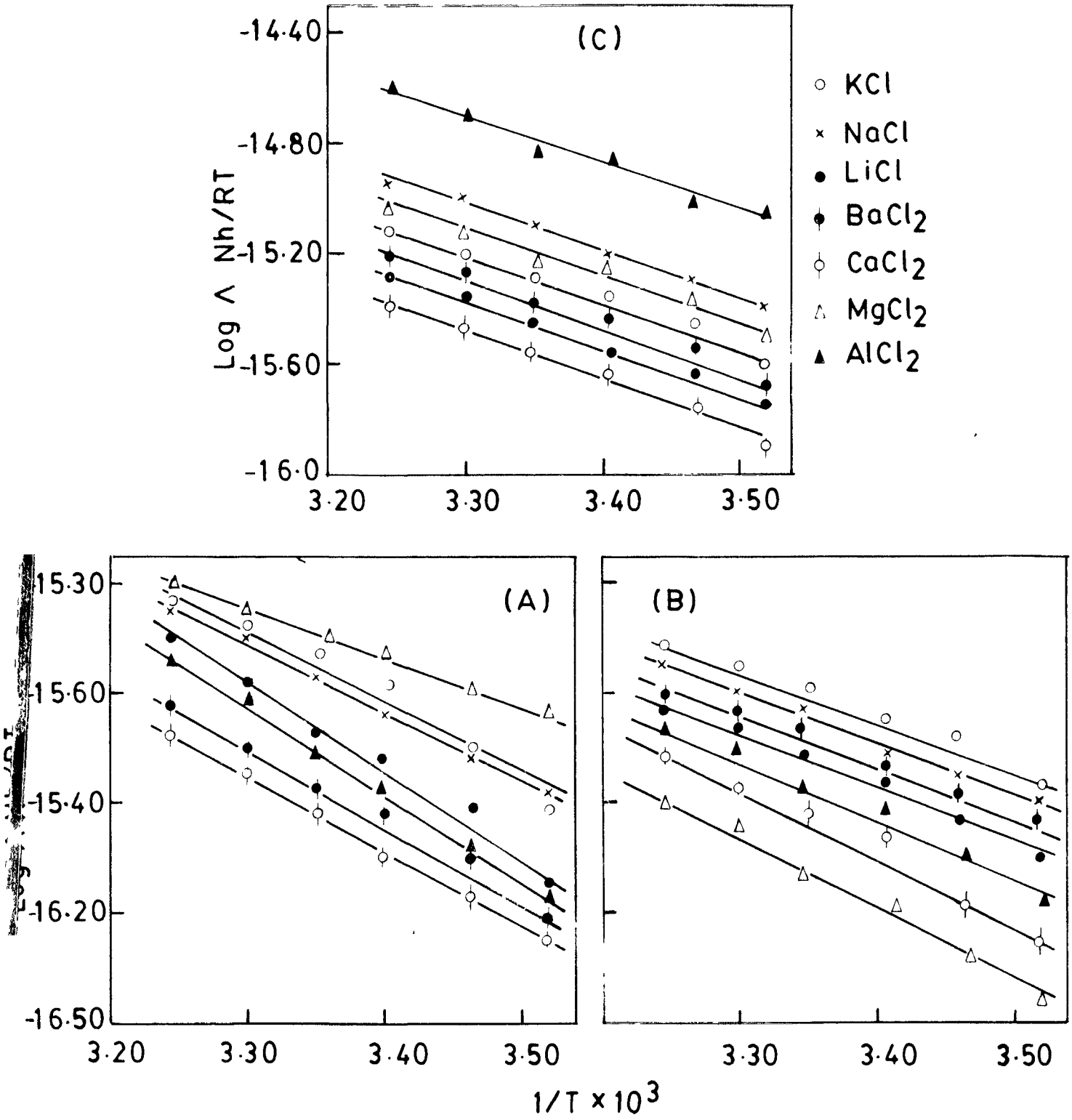

Fig.1·4: Plots of log Λ Nh/RT vs 1/T ×10^3 for various 1:1, 2:1 and 3:1 Electrolytes at 0·01M concentration across (A) Silver ferrocyanide, (B) Manganese ferrocyanide and (C) Cobalt ferrocyanide membranes.

where K is the Boltzman constant and d is the interionic jump distance i.e. the distance between equilibrium positions of diffusing species in the membrane. Equation 1.8 predicts that a plot of $\log \Lambda$ Vs $1/T$ gives straight line and E_a may be obtained (as described earlier). The values of E_a derived in this way are comparable to those derived by using eq. 1.5 - 1.7. Substituting the value of parameters $\Delta S^{\neq}$ and E_a in eqs. 1.8 and 1.9 (39) we get the value of interionic distance $\simeq 1.5$ Å. This value of d is not unusual of these systems (39). Various investigators (19-27, 37, 38, 40-42) have used value of d ranging from 1 to 5 A^0 for the membranes and various diffusing species. The values of various thermodynamic activation parameters, E_a, $\Delta H^{\neq}$, $\Delta F^{\neq}$ and $\Delta S^{\neq}$, derived in this way for the diffusion of various electrolytes in the membrane are given in Tables 1.22-1.42. These results indicate that the electrolyte permeation gives rise to negative values of $\Delta S^{\neq}$. According to Eyring and Co-workers (18,19), the values of $\Delta S^{\neq}$ indicate the mechanism of flow, large positive $\Delta S^{\neq}$ is interpreted to reflect breakage of bonds, while low values indicate that permeation has taken place without breaking bonds. The negative $\Delta S^{\neq}$ values are considered to indicate either formation of covalent bond between the permeating species and the membrane material or that

TABLE 1.22

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR POTASSIUM CHLORIDE ELECTROLYTE THROUGH SILVER FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a, Kcal	$\Delta H'$, Kcal	$\Delta F'$, Kcal	$\Delta S'$, e.u.
1×10^{-1}	8.40	5.00	10.00	-6.54
1×10^{-2}	9.21	5.50	10.30	-4.69
1×10^{-3}	10.45	6.10	10.00	-4.14
1×10^{-4}	11.40	7.20	11.00	-3.22

TABLE 1.23

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR POTASSIUM CHLORIDE ELECTROLYTE THROUGH MANGANESE FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a, Kcal	$\Delta H'$, Kcal	$\Delta F'$, Kcal	$\Delta S'$, e.u.
1×10^{-1}	5.75	2.50	9.90	-6.90
1×10^{-2}	6.50	2.95	9.85	-4.65
1×10^{-3}	7.45	3.30	10.35	-3.27
1×10^{-4}	8.42	3.75	10.70	-2.62

TABLE 1.24

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR POTASSIUM CHLORIDE ELECTROLYTE THROUGH COBALT FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'_f$ Kcal	$\Delta F'_f$ Kcal	$\Delta S'_f$ e.u.
1×10^{-1}	10.27	2.40	8.35	-9.16
1×10^{-2}	11.30	2.65	8.80	-6.21
1×10^{-3}	12.15	3.15	9.25	-4.65
1×10^{-4}	13.25	4.00	9.95	-3.45

TABLE 1.25

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR SODIUM CHLORIDE ELECTROLYTE THROUGH SILVER FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'_f$ Kcal	$\Delta F'_f$ Kcal	$\Delta S'_f$ e.u.
1×10^{-1}	7.60	3.32	9.75	-11.81
1×10^{-2}	8.20	3.72	10.15	- 8.38
1×10^{-3}	9.30	4.35	10.85	- 6.12
1×10^{-4}	10.15	4.80	11.20	- 5.20

TABLE 1.26

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR SODIUM CHLORIDE ELECTROLYTE THROUGH MANGANESE FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	9.21	4.16	9.95	-10.04
1×10^{-2}	10.35	4.50	10.30	- 7.50
1×10^{-3}	11.30	4.85	11.00	- 5.43
1×10^{-4}	12.10	5.20	11.50	- 4.37

TABLE 1.27

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR SODIUM CHLORIDE ELECTROLYTE THROUGH COBALT FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	6.71	3.12	9.30	-10.96
1×10^{-2}	7.69	3.95	9.65	- 8.65
1×10^{-3}	8.25	3.80	9.85	- 6.90
1×10^{-4}	9.30	4.30	10.30	- 4.60

TABLE 1.28

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR LITHIUM CHLORIDE ELECTROLYTE THROUGH SILVER FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	6.90	3.34	9.65	-9.21
1×10^{-2}	7.05	3.70	10.10	-6.90
1×10^{-3}	8.25	4.15	10.50	-5.90
1×10^{-4}	9.30	4.45	11.20	-5.06

TABLE 1.29

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR LITHIUM CHLORIDE ELECTROLYTE THROUGH MANGANESE FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	5.75	3.10	9.15	-8.75
1×10^{-2}	6.35	3.40	9.45	-6.80
1×10^{-3}	7.40	3.85	9.85	-5.82
1×10^{-4}	8.45	4.35	10.25	-4.80

TABLE 1.30

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR LITHIUM CHLORIDE ELECTROLYTE THROUGH COBALT FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a, Kcal	$\Delta H'_a$, Kcal	$\Delta F'_a$, Kcal	$\Delta S'_a$, e.u.
1×10^{-1}	7.69	2.70	8.45	-8.42
1×10^{-2}	8.15	2.99	8.80	-6.76
1×10^{-3}	9.30	3.30	9.30	-6.20
1×10^{-4}	10.40	3.70	9.75	-4.05

TABLE 1.31

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR BARIUM CHLORIDE ELECTROLYTE THROUGH SILVER FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a, Kcal	$\Delta H'_a$, Kcal	$\Delta F'_a$, Kcal	$\Delta S'_a$, e.u.
1×10^{-1}	10.13	4.90	8.80	-10.36
1×10^{-2}	11.25	5.38	10.38	-7.73
1×10^{-3}	12.10	5.80	10.56	-6.12
1×10^{-4}	13.90	6.10	10.65	-5.20

TABLE 1.32

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR BARIUM CHLORIDE ELECTROLYTE THROUGH MANGANESE FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	9.00	4.44	9.40	-9.01
1×10^{-2}	10.25	4.75	9.00	-6.07
1×10^{-3}	11.20	4.95	10.35	-4.60
1×10^{-4}	12.15	5.50	10.70	-2.99

TABLE 1.33

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR BARIUM CHLORIDE ELECTROLYTE THROUGH COBALT FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	12.30	5.22	10.50	-10.36
1×10^{-2}	12.95	5.55	10.95	- 6.67
1×10^{-3}	13.80	5.80	11.20	- 4.37
1×10^{-4}	14.20	6.30	11.80	- 2.99

TABLE 1.34

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR CALCIUM CHLORIDE ELECTROLYTE THROUGH SILVER FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	9.21	3.70	9.00	-0.21
1×10^{-2}	9.95	4.10	10.35	-6.35
1×10^{-3}	10.00	4.55	10.65	-5.75
1×10^{-4}	11.35	4.90	11.15	-4.97

TABLE 1.35

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR CALCIUM CHLORIDE ELECTROLYTE THROUGH MANGANESE FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	7.50	4.16	10.28	-0.87
1×10^{-2}	8.35	4.55	10.65	-6.07
1×10^{-3}	9.15	4.87	10.97	-6.15
1×10^{-4}	10.40	5.30	11.38	-4.60

TABLE 1.36

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR CALCIUM CHLORIDE ELECTROLYTE THROUGH COBALT FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	12.10	4.82	10.35	-0.38
1×10^{-2}	12.65	5.25	10.70	-5.75
1×10^{-3}	13.45	5.63	11.10	-4.37
1×10^{-4}	14.20	5.95	11.40	-3.45

TABLE 1.37

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR MAGNESIUM CHLORIDE ELECTROLYTE THROUGH SILVER FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	5.19	3.22	9.55	-7.83
1×10^{-2}	6.35	3.55	9.80	-6.98
1×10^{-3}	7.20	3.97	10.15	-5.08
1×10^{-4}	8.40	4.25	10.45	-4.37

TABLE 1.38

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR MAGNESIUM CHLORIDE ELECTROLYTE THROUGH MANGANESE FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a, Kcal	$\Delta H'$, Kcal	$\Delta F'$, Kcal	$\Delta S'$, e.u.
1×10^{-1}	4.70	5.30	10.75	-10.96
1×10^{-2}	5.50	5.02	11.20	- 6.21
1×10^{-3}	6.25	6.25	11.55	- 4.60
1×10^{-4}	7.05	6.60	11.00	- 3.45

TABLE 1.39

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR MAGNESIUM CHLORIDE ELECTROLYTE THROUGH COBALT FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a, Kcal	$\Delta H'$, Kcal	$\Delta F'$, Kcal	$\Delta S'$, e.u.
1×10^{-1}	5.61	3.84	9.90	-0.21
1×10^{-2}	6.25	4.20	10.30	-6.21
1×10^{-3}	7.38	4.55	10.70	-4.60
1×10^{-4}	8.18	4.90	11.10	-3.45

TABLE 1.40

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR ALUMINIUM CHLORIDE ELECTROLYTE THROUGH SILVER FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a, Kcal	$\Delta H'$, Kcal	$\Delta F'$, Kcal	$\Delta S'$, e.u.
1×10^{-1}	9.21	4.90	9.95	-7.83
1×10^{-2}	9.80	5.25	10.40	-6.90
1×10^{-3}	10.50	5.55	10.75	-5.90
1×10^{-4}	11.15	5.05	11.20	-6.52

TABLE 1.41

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR ALUMINIUM CHLORIDE ELECTROLYTE THROUGH MANGANESE FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a, Kcal	$\Delta H'$, Kcal	$\Delta F'$, Kcal	$\Delta S'$, e.u.
1×10^{-1}	7.00	4.10	9.48	-8.67
1×10^{-2}	7.90	4.60	9.90	-8.06
1×10^{-3}	8.35	4.90	10.30	-6.21
1×10^{-4}	9.65	5.30	10.65	-6.75

TABLE 1.42

VALUES FOR ACTIVATION ENERGY E_a AND OTHER THERMODYNAMIC PARAMETERS CALCULATED FROM THE TRANSITION STATE THEORY OF RATE PROCESSES FOR ALUMINIUM CHLORIDE ELECTROLYTE THROUGH COBALT FERROCYANIDE MEMBRANE (Temperature = 25°C)

Parameters Concentration (Mol/l)	E_a Kcal	$\Delta H'$ Kcal	$\Delta F'$ Kcal	$\Delta S'$ e.u.
1×10^{-1}	5.20	3.32	8.70	-8.38
1×10^{-2}	6.30	3.65	9.40	-8.90
1×10^{-3}	7.15	3.90	9.05	-4.97
1×10^{-4}	8.35	4.35	10.45	-4.51

the permeation through the membrane may not be the rate determining step.

On the contrary, Barrer (37, 43, 44) has developed the concept of "zone activation" and applied it to the permeation of gases through polymer membranes. According to this zone hypothesis, a high $\Delta S^{\neq}$, which has been correlated with high energy of activation or the reversible loosening of more chain segments of the membrane. A low $\Delta S^{\neq}$ then means either a small zone of activation or no loosening of the membrane structure on the permeation. In view of these differences in the interpretation of $\Delta S^{\neq}$, Shuler et. al. (20) who found negative values of $\Delta S^{\neq}$ for ether permeation through collodion membranes, have stated that "it would probably be correct to interpret the small negative values of $\Delta S^{\neq}$ mechanically as interstitial permeation of the membrane (minimum chain loosening) with partial immobilization in the membrane (small zone of disorder)". On the other hand, Tien and Ting (21) who found negative $\Delta S^{\neq}$ values for the permeation of water through very thin (50 A^{0} thickness) bilayer membrane, stressed the possibility that the membrane may not be the rate determining step but solution- membrane interface was the limiting step for permeation.

The result of all these investigations are that the membrane conductance can be determined at different temperatures with reasonable accuracy. The membranes are weakly charged and ionic species retain their hydration shell at least partially while diffusing through membrane pores. Negative $\Delta g^{\#}$ values suggest that the partial immobilization of ion takes place most probably due to interstitial permeation and ionic interaction with the fixed charge groups of the membrane skeleton. The interionic distance (or jump distance) of the system under study is of the order of 1.5 A^{0} which is consistant with the empirical values chosen by various investigators (19-27, 37, 38, 40-42).

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Membrane Potential and Evaluation of Charge Density:

One of the most consistent properties of biological system is the presence of a voltage across the cellular surfaces. The mechanism whereby this potential arises is still in dispute. Some consider it to be a diffusional potential while others suggest the voltage to be an adsorption potential (1). The findings that the potential was same as the liquid junction potential if the membrane carried no fixed charge, and that the magnitude of the external solution and the sign of the fixed charge in the case of the membrane carried some charge, has led Teorell (2,3); Meyers and Sievers (4) to formulate simultaneously a theory based on fixed charge concept which is still regarded as the most pertinent starting point for the investigation of the actual mechanisms of the ionic or molecular processes which occur in the membrane phase. In recent years, based on fixed charge concept a number of theoretical approaches have been made to calculate the emf of the system solution-membrane-solution and were examined for their validity employing model systems.

In this chapter, we described the preparation of polystyrene based stannous ferrocyanide, stannic ferro-

cyanide and stannic phosphate membranes to be possibly utilized as a model for biological and theoretical studies. The membranes may suitably be used in the fuel cells, in nuclear technology, in the electrodialysis at high temperature and in several processes where strong oxidizing solutions are employed. The thermodynamically effective fixed charge density which is an important characteristic governing the membrane phenomena have been evaluated from the membrane potential measurements using the widely accepted theory of Teorell (2,3); Meyer and Sievers (4), and the most recently developed theories of Kobatake et al. (5-16) and Tanaka et al. (17) based on the principle of irreversible thermodynamics.

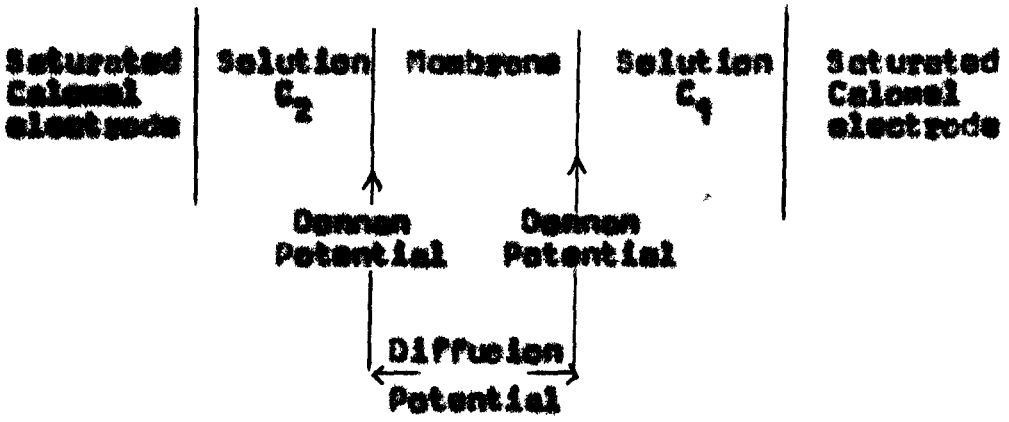
EXPERIMENTAL PROCEDURE

The polystyrene based membrane were prepared by the method based on U. S. Patent No. 2814, 976. Stannic phosphate precipitate was prepared by mixing 0.05 M aqueous solutions of stannic chloride and sodium dihydrogen orthophosphate. The precipitate was digested at room temperature for 24 hr, filtered, washed, dried at 40 °C and ground to powder. It was then mixed with 25% polystyrene previously ground to less than 200 mesh size. 2 g of this mixture was transferred to a die fitted with automatic hydraulic press and temperature control (Apex hydraulic press type H_1) serial No. A/205413, London, England). The die was first brought to 60 °C and then a pressure of 6,000 psi was applied. After 5 minutes the pressure was released and the pellet was taken out. The optimum condition to get a membrane of suitable mechanical strength was obtained by using different ratios of polystyrene and gel and varying temperature and pressure. e.g. stannic phosphate membrane was prepared by embedding 25% polystyrene by the application of 6,000 psi at 60 °C. Those containing larger amount of binder did not give reproducible results while those having lesser amount were quite

unstable. Other membranes were prepared following the similar procedure. The requisite electrolyte solutions and the conditions necessary for the preparation of the membranes are given below

Membrane	Solution (1)	Solution (2)	Temp	Press	% of polystyrene
1) Stannous Ferrocyanide	Stannous Chloride	Potassium Ferrocyanide	30°C	5,000 Psi	25
2) Stannic Ferrocyanide	Stannic Chloride	Potassium Ferrocyanide	30°C	5,000 Psi	25

The membrane thus prepared were 0.15 Cm thick. It was fixed at one end of a glass tube using Araldite, an adhesive (CIBA Bombay, India). Electrochemical cells of the type



were set up for measuring membrane potentials. A

tenfold difference in concentration, $C_2 / C_1 = 10$, of the chlorides of potassium, sodium and lithium solutions across the membrane were taken. The whole cell assembly was kept in a thermostat maintained at $25 \pm 0.1\ ^{\circ}C$. The potentials were monitored using a pye-precision vernier potentiometer (No.7560). All the electrolyte solutions used in the investigation were prepared from the analytical grade reagents (BDH) and deionized water.

RESULTS AND DISCUSSION

The values of membrane potential measured across polystyrene based stannous ferrocyanide, stannic ferrocyanide and stannic phosphate membranes in contact with different concentrations of various 1:1 electrolytes are given in Tables 2.1 – 2.3 and are also plotted in Fig. 2.1 (a, b and c) against log $(C_1 + C_2)/2$.

The inorganic precipitate membranes have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations (18-29). This property is attributed to the presence of a net charge on the membrane probably due to adsorption of anions or cations. The quantity of charge required to generate potentials, particularly when dilute solutions are used, is small. This, of course, is dependent on the porosity of the membrane. If the membrane pores are too wide, any amount of charge on the membrane does little to generate good potentials. But if the membrane pores are narrow, a little charge on it can give ideal potentials according to the Nernst equation

$$E_{mem} = \frac{RT}{F} \ln \frac{a_1}{a_2} \qquad (2.1)$$

where a_1 and a_2 are the activities of the two solutions

TABLE 2.1

THE VALUES OF THE OBSERVED MEMBRANE POTENTIAL E_m(mV) ACROSS STANNOUS FERROCYANIDE MEMBRANE AT 25 ± 0.1°C

Electrolyte Concentration C_2/C_1(Mol/l)	KCl	NaCl	LiCl
$1/1 \times 10^{-1}$	0.4	1.8	4.6
$5 \times 10^{-1} / 5 \times 10^{-2}$	5.8	6.7	8.4
$1 \times 10^{-1} / 1 \times 10^{-2}$	13.9	11.9	14.2
$5 \times 10^{-2} / 5 \times 10^{-3}$	23.0	20.6	21.6
$1 \times 10^{-2} / 1 \times 10^{-3}$	34.5	31.8	33.3
$5 \times 10^{-3} / 5 \times 10^{-4}$	44.3	40.7	39.0
$1 \times 10^{-3} / 1 \times 10^{-4}$	54.7	48.7	45.0

Vide Fig. 2.1(a)

TABLE 2.2

THE VALUES OF THE OBSERVED MEMBRANE POTENTIAL E_m(mV) ACROSS STANNIC FERROCYANIDE MEMBRANE AT 25 ± 0.1°C

Electrolyte Concentration C_2/C_1(Mol/l)	KCl	NaCl	LiCl
$1/1 \times 10^{-1}$	5.2	8.4	3.3
$5 \times 10^{-1} / 5 \times 10^{-2}$	15.8	14.5	10.8
$1 \times 10^{-1} / 1 \times 10^{-2}$	25.4	22.3	16.9
$5 \times 10^{-2} / 5 \times 10^{-3}$	36.0	29.5	26.7
$1 \times 10^{-2} / 1 \times 10^{-3}$	44.7	39.8	37.4
$5 \times 10^{-3} / 5 \times 10^{-4}$	50.3	51.9	47.8
$1 \times 10^{-3} / 1 \times 10^{-4}$	56.8	58.6	51.1

Vide Fig. 2.1(b)

TABLE 3.3

THE VALUES OF THE OBSERVED MEMBRANE POTENTIAL E_m(mV) ACROSS STATIC PHOSPHATE MEMBRANE AT 25 ± 0.1°C

Electrolyte Concentration C_2/C_1(Mol/ℓ)	KCl	NaCl	LiCl
$1 / 1 \times 10^{-1}$	7.2	7.7	4.7
$5 \times 10^{-1} / 5 \times 10^{-2}$	12.1	10.8	0.2
$1 \times 10^{-1} / 1 \times 10^{-2}$	18.3	17.0	15.0
$5 \times 10^{-2} / 5 \times 10^{-3}$	26.0	25.2	21.2
$1 \times 10^{-2} / 1 \times 10^{-3}$	37.8	34.6	27.0
$5 \times 10^{-3} / 5 \times 10^{-4}$	46.0	42.9	33.8
$1 \times 10^{-3} / 1 \times 10^{-4}$	51.8	48.7	41.2

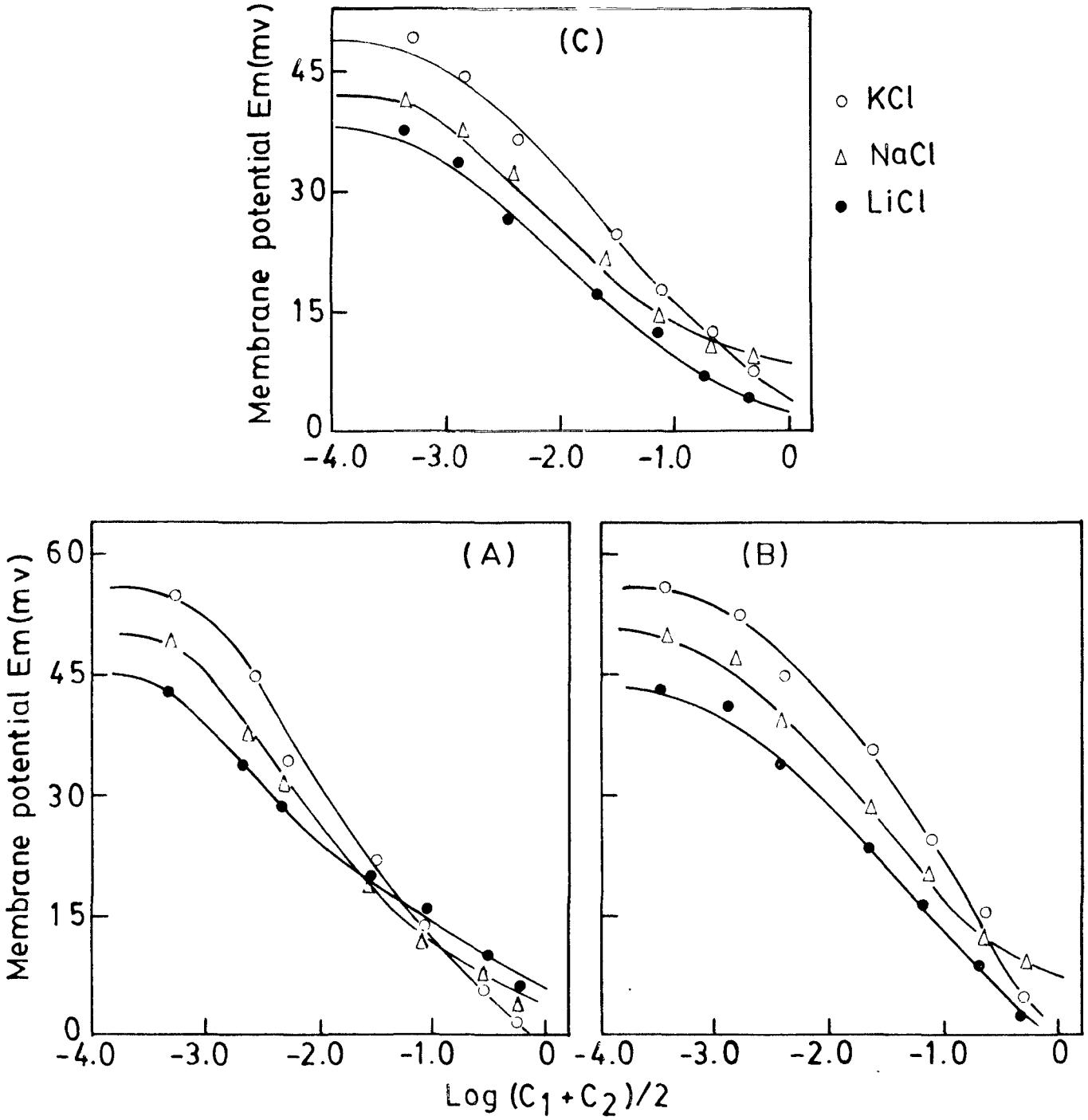


Fig. 2·1: Plots of membrane potential Em(mv) against log $(C_1 + C_2)/2$ using 1:1 Electrolytes across (A) Stannous ferrocyanide, (B) Stannic ferrocyanide and (C) Stannic phosphate membranes.

on either side of the membrane, E_{mem} is the membrane potential, and R, T and F have their usual significance.

The fixed group present in a well characterized ion exchange membrane can easily be estimated by titration (30). Lakshminarayaniah (31), used the isotopic and potentiometric methods to evaluate the apparent fixed charge on perlodion membranes. In this study, the titration method proved inconvenient and inaccurate, and the isotopic method was discarded in view of the strong ionic adsorption phenomenon exhibited by the system. Consequently the potentiometric method based on the fixed charge concept of Teorell (2, 3) and Meyer and Sievers (4), the important features of which have been reviewed by Lakshminarayaniah (32), was used.

According to this theory, total membrane potential is considered to be made up of a diffusion potential within the membrane and interfacial (Donnan) potentials at the membrane solution interfaces. The total membrane potential E_m in millivolts according to this theory,

applicable to a highly idealized system is given by the equation at 25°C

$$E_m = 59.2 \left[\log \frac{C_2}{C_1} \frac{(4C_1^2 + X^2)^{\frac{1}{2}} + X)}{(4C_2^2 + X^2)^{\frac{1}{2}} + X)} + U \log \frac{(4C_2^2+X^2)^{\frac{1}{2}}+XU}{(4C_1^2+X^2)^{\frac{1}{2}}+XU} \right]$$

.... (2.2)

where $U = (\bar{U} - \bar{V})/(\bar{U} + \bar{V})$, $\bar{U}$ and $\bar{V}$ are the mobilities of the cation and anion respectively, in the membrane expressed in equivalents / litre of imbibed solution. In order to evaluate this parameter for the simple case of 1:1 electrolyte and membrane carrying a net negative charge of unity ($X = 1$), theoretical concentration potential E_m across the membrane were calculated as function of C_2 the ratio (C_2 / C_1) being kept at a constant value of 10 for different mobility ratios $\bar{U} / \bar{V}$. The values of E_m thus calculated are given in Table 2.4. The observed membrane potential values are also plotted in the same graph as a function of log ($1 / C_2$). The experimental curve is shifted horizontally until it coincides with one of the theoretical curves. The extent of this shift gives log X and the parallel theoretical curve the value $\bar{U} / \bar{V}$. The values of X and $\bar{U} / \bar{V}$ so derived for various membranes are given in Table 2.5.

TABLE 2.4

THEORETICAL VALUES OF MEMBRANE POTENTIALS E_D(mV) CALCULATED FROM TEORELL-MEYER-SIEVERS METHOD FOR DIFFERENT MOBILITY RATIO $\bar{U}/\bar{V}$ AND ($\bar{X} = 1$) AT DIFFERENT CONCENTRATIONS

Mobility ratio $\bar{U}/\bar{V}$ Concentration C_2/C_1(Mol/l)	1.0	1.2	1.4	1.6	1.8	2.0
$1 \times 10^{-1} / 1$	15.3	16.1	20.2	23.5	26.8	30.0
$5 / 5 \times 10^{-1}$	40.7	20.1	30.2	30.0	32.3	35.2
$1 / 1 \times 10^{-1}$	45.0	34.0	37.5	45.2	48.7	50.0
$5 \times 10^{-1} / 5 \times 10^{-2}$	50.2	50.0	53.0	55.0	57.0	58.0
$1 \times 10^{-1} / 1 \times 10^{-2}$	55.0	55.0	57.0	58.8	59.0	59.5
$5 \times 10^{-2} / 5 \times 10^{-3}$	59.0	59.2	59.4	60.0	60.0	60.0
$1 \times 10^{-2} / 1 \times 10^{-3}$	59.9	59.9	60.0	60.0	60.0	60.0
$5 \times 10^{-3} / 5 \times 10^{-4}$	60.0	60.0	60.0	60.0	60.0	60.0
$2 \times 10^{-3} / 1 \times 10^{-4}$	60.0	60.0	60.0	60.0	60.0	60.0

TABLE 2.5

VALUES OF MEMBRANE CHARGE DENSITY $\bar{X}$ (eq/ℓ), MOBILITY RATIO ($\bar{U}$ / U) FOR VARIOUS MEMBRANE ELECTROLYTE SYSTEMS USING TEORELL-MEYER-SIEVERS THEORY AT 25 ± 0.1°C

Electrolyte / Membrane	Parameters	KCl	BaCl	LiCl
Stannous ferrocyanide	$(\bar{X})\times10^{3}$	7.9	6.2	5.2
	($\bar{U}$ / U)	1.0	1.2	1.2
Stannic ferrocyanide	$(\bar{X})\times10^{3}$	8.3	7.0	6.4
	($\bar{U}$ / U)	1.2	1.2	1.0
Stannic phosphate	$(\bar{X})\times10^{3}$	8.2	7.4	5.0
	($\bar{U}$ / U)	1.2	1.0	1.0

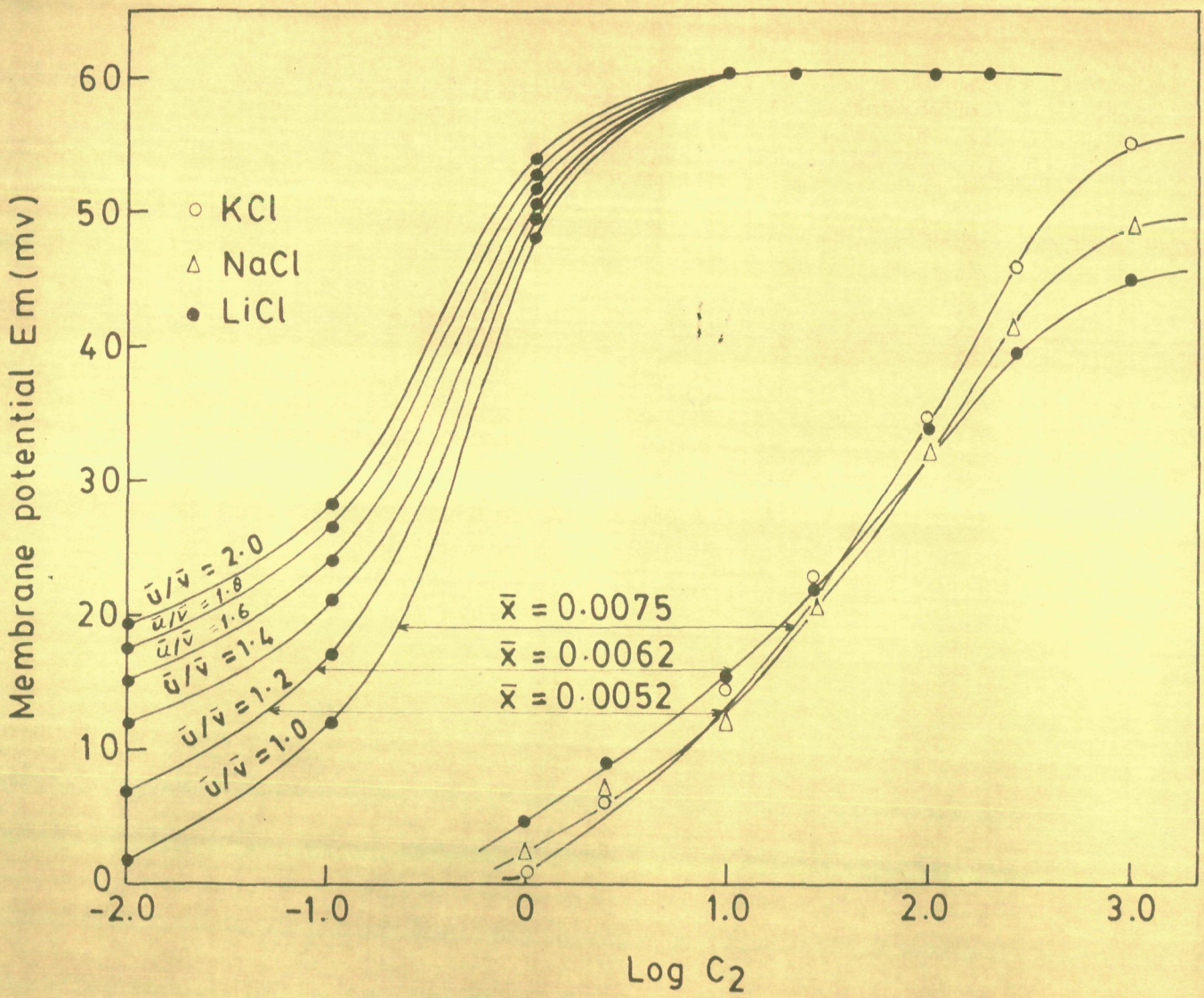


Fig. 2·2: Plots of membrane potential vs. log C_2 with various 1:1 electrolytes. Smooth curves are the theoretical membrane potential at different mobility ratios and dotted curves are the observed membrane potential across stannous ferrocyanide membrane.

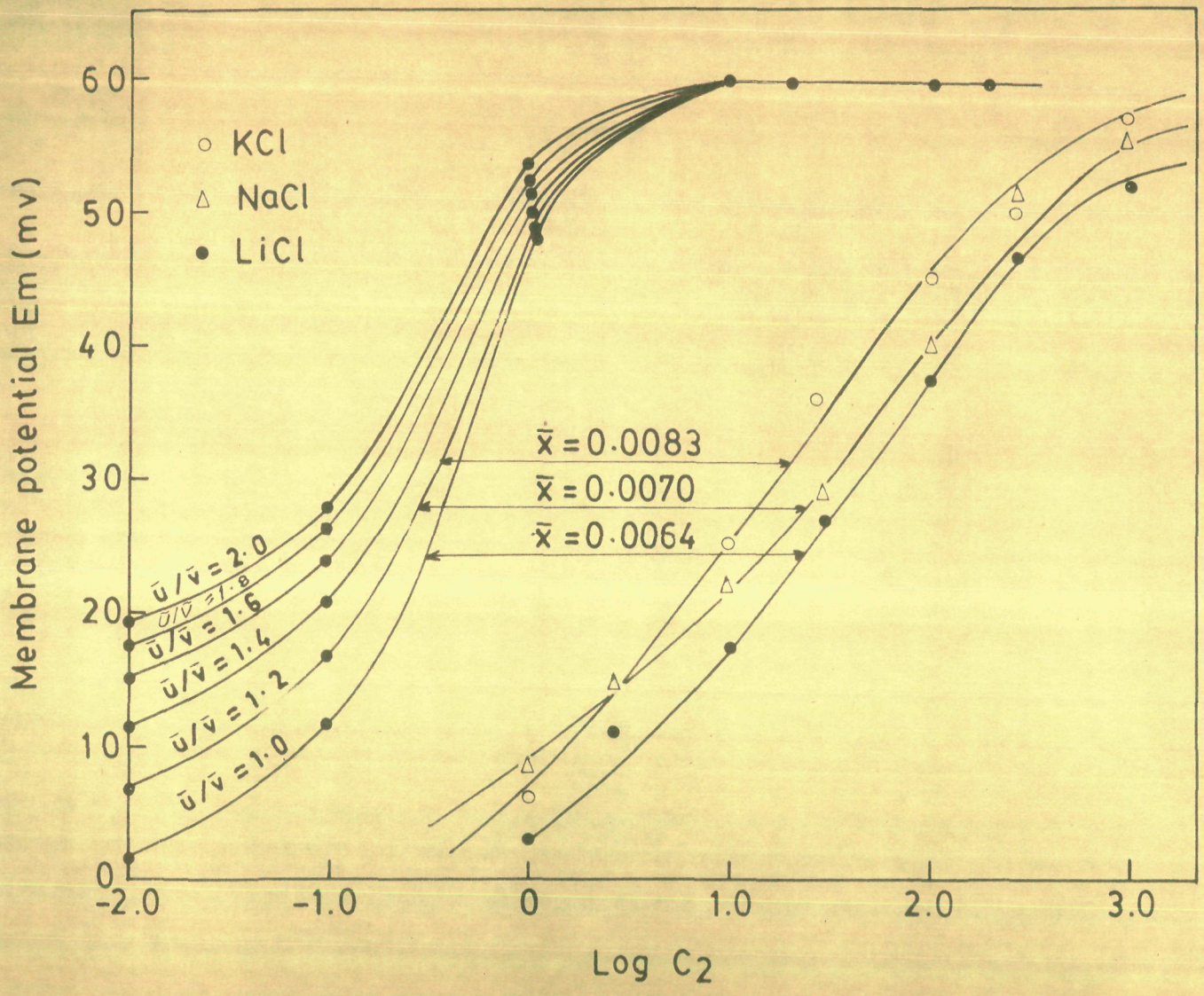


Fig. 2·3: Plots of membrane potential vs. log C_2 with various 1:1 electrolytes. Smooth curves are the theoretical membrane potential at different mobility ratios and dotted curves are the observed membrane potential across stannic ferrocyanide membrane.

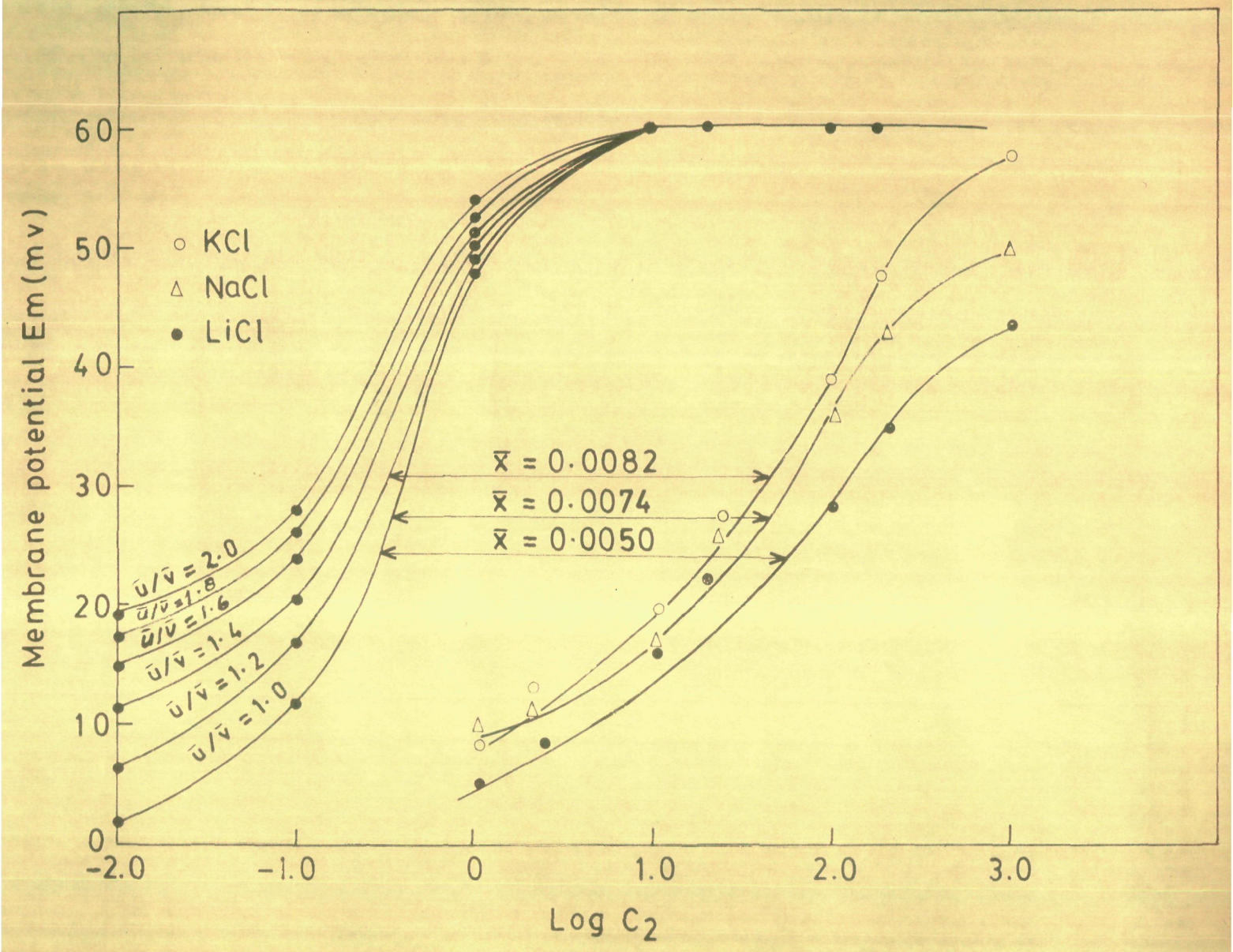


Fig.2.4: Plots of membrane potential vs. log C_2 with various 1:1 electrolyte. Smooth curves are the theoretical membrane potential at different mobility ratios and dotted curves are the observed membrane potential across stannic phosphate membrane.

Using the fixed charge concept of Teorell-Meyer-Sievers (TMS) theory (2-4) and the basic flux equations provided by the nonequilibrium thermodynamics, Kobatake and Cu-eachara (5-16) have derived the following expression for membrane potential E_m.

$$E_m = -\frac{RT}{F}\left[1/\beta \ln \frac{c_2}{c_1} - (1+\frac{1}{\beta} - 2\alpha) \ln \left(\frac{c_2 + \alpha\beta\overline{X}}{c_1 + \alpha\beta\overline{X}} \right) \right] \quad (2.3)$$

where $\alpha = u / (u+v)$; $\beta = 1 + (K\overline{X} / u)$; and K is a constant dependent upon the viscosity of the polymer network of which the membrane is composed. Other symbols have their usual significance. To evaluate the membrane parameters α, β and $\overline{X}$, two limiting forms of eqn. 2.3 were derived. When the external salt concentration c is sufficiently small,

$$\left| \overline{E}_m \right| = \frac{1}{\beta} \ln\gamma - \left(\frac{\gamma - 1}{\alpha\beta\gamma} \right)(1 + \frac{1}{\beta} - 2\alpha)\left(\frac{c_2}{\overline{X}} \right) + \ldots (2.4)$$

where $\left| \overline{E}_m \right| = F E_m / RT$

and $\gamma = c_2 / c_1$

When the salt concentration c is high,

$$1 / t_{-m} = \frac{1}{1-\alpha} + \frac{(\ln\beta - \alpha(\beta))(\gamma - 1)}{2 (1-\alpha)^2 \ln\gamma} \left(\frac{\overline{X}}{c_2} \right) + \quad \ldots (2.5)$$

Here t_{-m} is apparent transference number of anion (anion)

in a negatively charged membrane defined by

$$/ \bar{\zeta}_m / = (1-2 t_-) \ln C_2 / C_1 \qquad (2.6)$$

The values of t_- calculated from observed membrane potentials using eqn 2.6 are given in Tables 2.6 - 2.8. Equation 2.4 was used to give the value of β, and a relation between αc and $\bar{X}$ by evaluating the intercept and the initial slope of the plot of $/ \bar{\zeta}_m /$ against C_2 (Fig. 2.5 a, b and c), while equation 2.5 was used to evaluate αc from the intercept of a plot of $1 / t_-$ against $1 / C_2$ (Fig. 2.6 a, b and c). The values of $\bar{X}$ were then determined by inserting this value of αc in the relation between αc and $\bar{X}$ obtained earlier. The values of αc , β , and $\bar{X}$ derived in this way for the membranes and 1:1 electrolytes are given in Table 2.9, 2.10.

Once the values of the parameters αc , β and $\bar{X}$ for a given membrane-electrolyte system have been determined, one can get the theoretical $\bar{\zeta}_m$ vs. C_2 curves using equation 2.3 for any given γ ($= C_2 / C_1$) and compare it with the corresponding experimental data. For this comparison equation 2.3 can be rewritten in the following form as suggested by Kobatake and Toyoshima (1966)

$$\frac{f(\gamma, \alpha, \beta)}{(\alpha c)} = z \qquad (2.7)$$

with q and z defined by

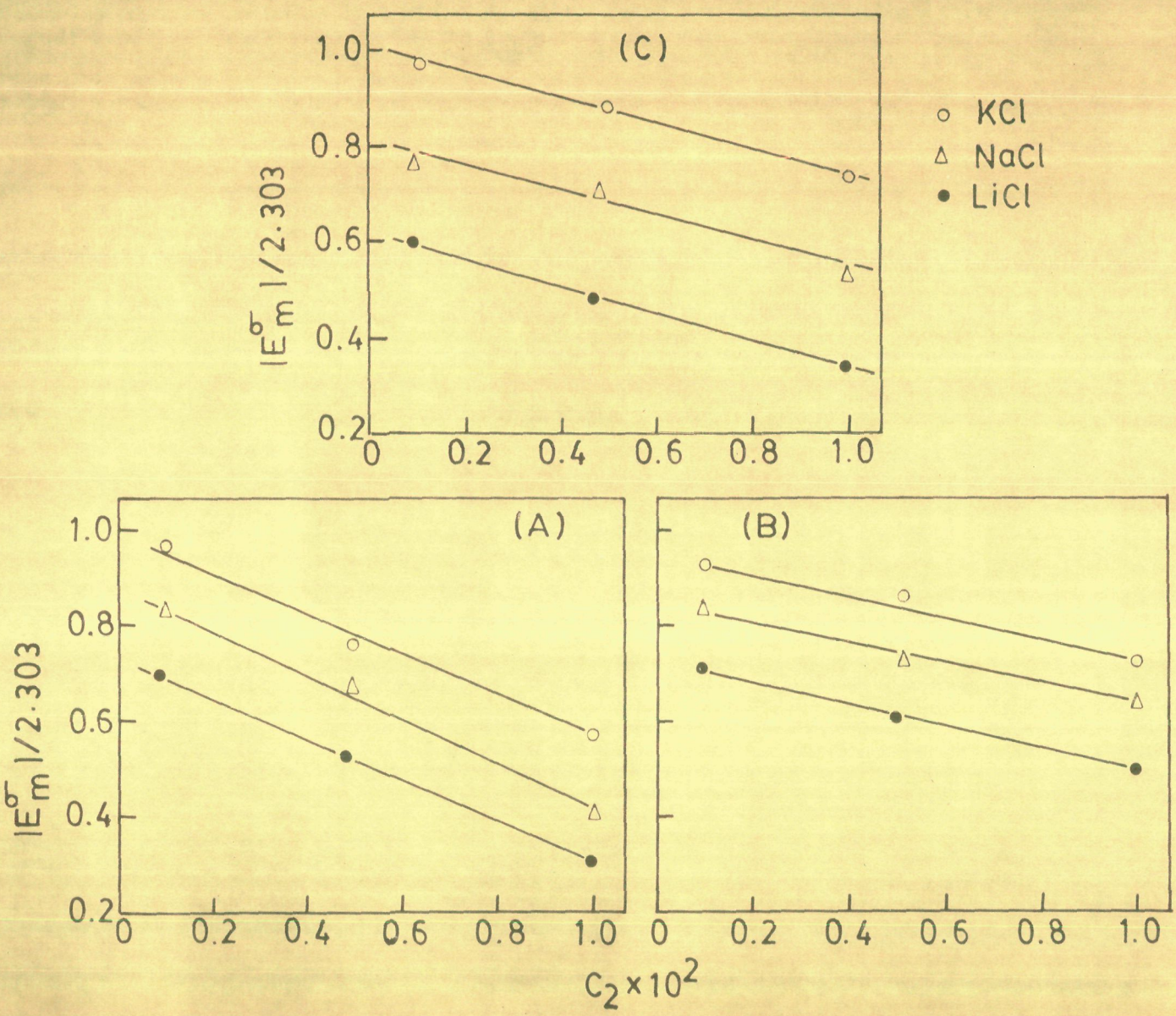


Fig. 2·5: Plots of $|E_m^\sigma|/2.303$ against C_2 for (A) Stannous ferrocyanide, (B) Stannic ferrocyanide and (C) Stannic phosphate membranes.

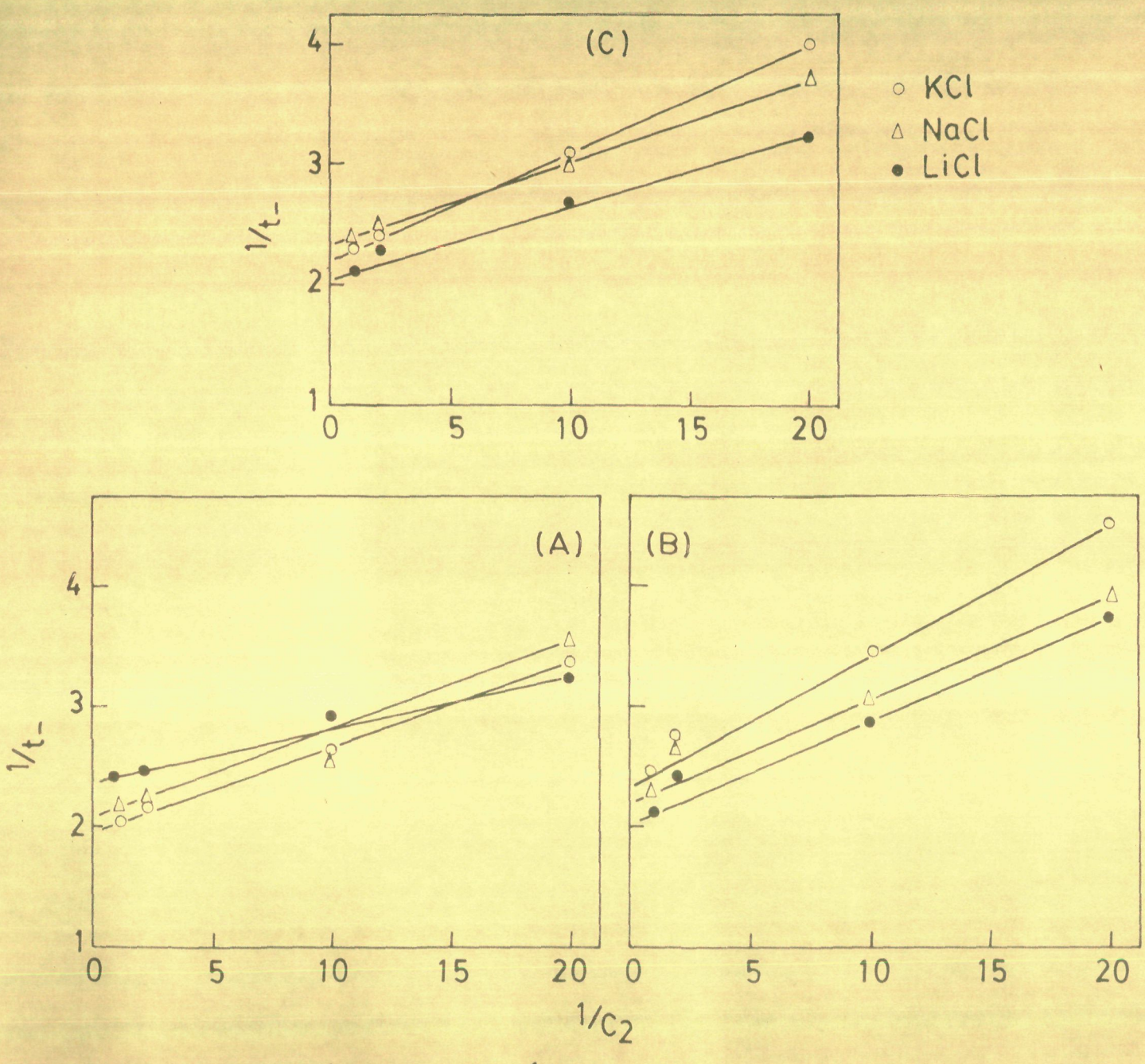


Fig.2·6: Plots of $^{1}/_{t_-}$ against $^{1}/C_2$ for (A) Stannous ferrocyanide, (B) Stannic ferrocyanide and (C) Stannic phosphate membranes using 1:1 Electrolyte solutions at constant r (r = 10).

TABLE 2.6

TRANSFERENCE NUMBER t_- OF IONS DERIVED FROM OBSERVED MEMBRANE POTENTIAL AT VARIOUS ELECTROLYTE CONCENTRATION THROUGH STANNOUS FERROCYANIDE MEMBRANE

Electrolyte Concentration C_2/C_1 (Mol/l)	KCl	NaCl	LiCl
$1 / 1 \times 10^{-1}$	0.43	0.40	0.42
$5 \times 10^{-1} / 5 \times 10^{-2}$	0.45	0.44	0.40
$1 \times 10^{-1} / 1 \times 10^{-2}$	0.39	0.39	0.38
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.30	0.32	0.31
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.21	0.23	0.21
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.12	0.15	0.17
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.03	0.08	0.11

Vide Fig. 2.6(a)

TABLE 2.7

TRANSFERENCE NUMBER t_- OF IONS DERIVED FROM OBSERVED MEMBRANE POTENTIAL AT VARIOUS ELECTROLYTE CONCENTRATION THROUGH STANNIC FERROCYANIDE MEMBRANE

Electrolyte Concentration C_2/C_1 (Mol/l)	KCl	NaCl	LiCl
$1 / 1 \times 10^{-1}$	0.40	0.44	0.47
$5 \times 10^{-1} / 5 \times 10^{-2}$	0.36	0.37	0.40
$1 \times 10^{-1} / 1 \times 10^{-2}$	0.28	0.31	0.36
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.19	0.23	0.27
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.12	0.16	0.18
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.07	0.08	0.09
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.01	0.03	0.05

Vide Fig. 2.6(b)

TABLE 2.8

TRANSFERENCE NUMBER t_- OF COIONS DERIVED FROM OBSERVED MEMBRANE POTENTIAL AT VARIOUS ELECTROLYTE CONCENTRATION THROUGH STARCH PHOSPHATE MEMBRANE

Electrolyte Concentration C_2/C_1 (Mol/l)	KCl	NaCl	LiCl
$1 / 1 \times 10^{-1}$	0.43	0.43	0.40
$5 \times 10^{-1} / 5 \times 10^{-2}$	0.39	0.41	0.43
$1 \times 10^{-1} / 1 \times 10^{-2}$	0.30	0.35	0.37
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.20	0.28	0.32
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.18	0.20	0.27
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.11	0.14	0.21
$1 \times 10^{-3} / 1 \times 10^{-4}$	[illegible]	[illegible]	0.15

Vide Fig. 2.6(e)

TABLE 2.2

VALUES OF THE MEMBRANE PARAMETERS α AND β FOR VARIOUS MEMBRANE ELECTROLYTE SYSTEMS AT $\gamma = 10$

Electrolyte	KCl		NaCl		LiCl	
Membrane	α	β	α	β	α	β
Stannous Ferrocyanide	0.50	2.2	0.52	2.1	0.56	2.4
Stannic Ferrocyanide	0.56	4.0	0.53	4.7	0.50	5.0
Stannic Phosphate	0.40	1.1	0.42	1.2	0.34	1.4

Table 2.10

VALUES OF THE EFFECTIVE FIXED CHARGE DENSITY $\bar{X}$ (eq/l) USING KOBATAKE'S METHOD FOR VARIOUS MEMBRANE ELECTROLYTE SYSTEMS AT 25 ± 0.1°C

Electrolyte Membrane	KCl	NaCl	LiCl
Stannous Ferrocyanide			
$(\bar{X})\times10^3$, eq/l	7.0	6.6	5.5
Stannic Ferrocyanide			
$(\bar{X})\times10^3$, eq/l	8.0	7.5	6.6
Stannic Phosphate			
$(\bar{X})\times10^3$, eq/l	8.9	8.0	5.6

$$q = \frac{|\bar{\zeta}| + (1-2\alpha)\ln\gamma}{\sqrt{\beta^2 + (1-2\alpha)^2}} \qquad (2.8)$$

and $Z = \zeta_m / \alpha\beta\bar{X}$ (2.9)

Thus if equation 2.7 is valid, the value of $(\gamma - e^q)/(e^q - 1)$ calculated from the predetermined values of α, β and $\bar{X}$ through measured membrane potential ζ_m, for a particular value of γ must fall on a straight line which should have a unit slope and pass the co-ordinate origin when plotted against Z. This behaviour should be observed irrespective of the value of γ and the kind of membrane-electrolyte system used. Fig. 2.7 (a,b and c) demonstrate that the theoretical prediction of equation 2.7 is borne out quite satisfactorily by our experimental results with all the polystyrene based inorganic precipitate membranes.

Kobatake and Kawa (13) derived another equation 2.10 for the membrane potential starting with the basic flow equation provided by the thermodynamics of irreversible processes and using a different set of assumptions: namely, (a) the contribution of ions movement is negligible (12), and (b) small ions do not behave ideally in a charged membrane (13). Their result is

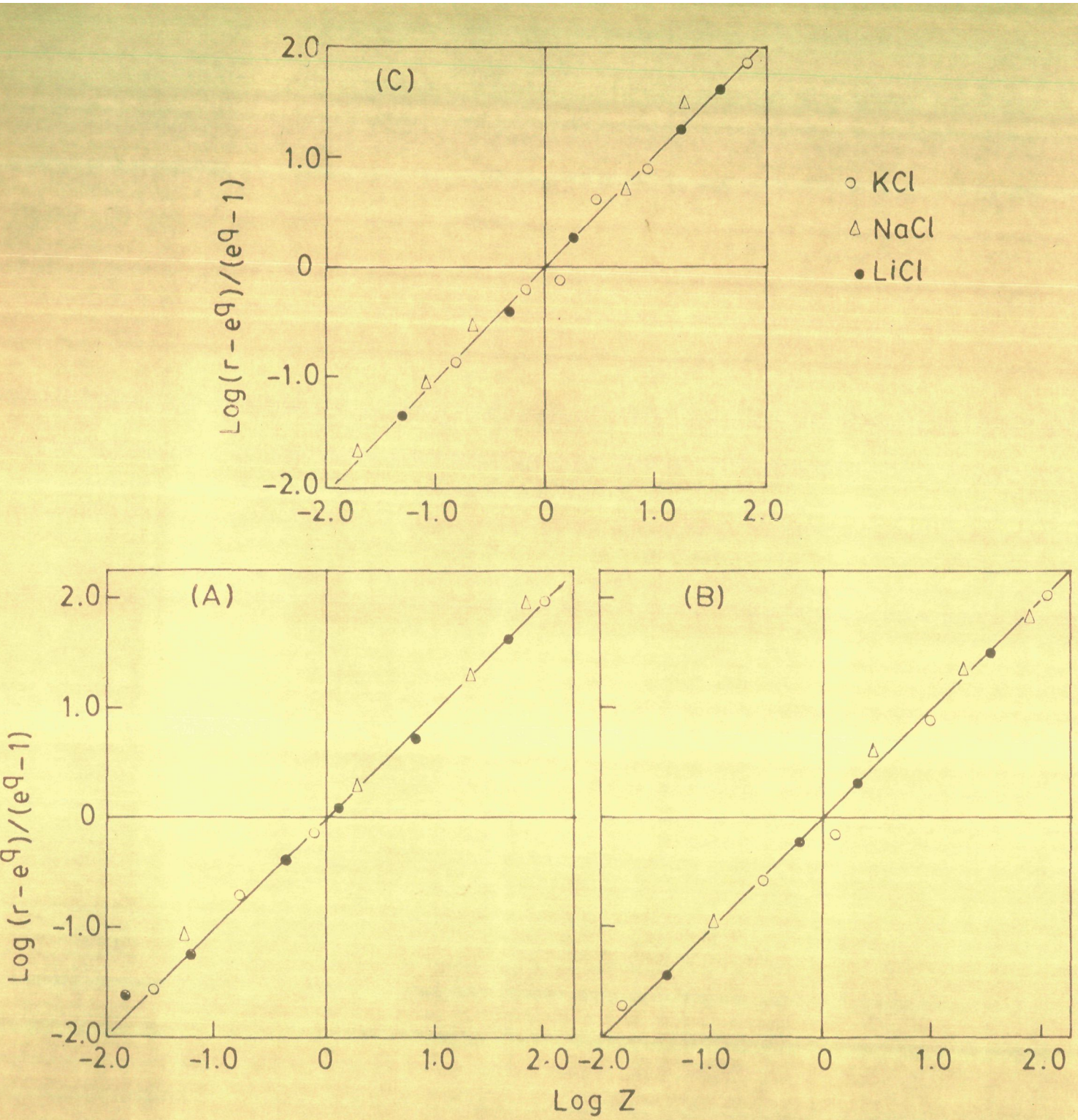


Fig. 2·7: Plots of log $(r - e^q)/(e^q - 1)$ against log Z for (A) Stannous ferrocyanide, (B) Stannic ferrocyanide and (C) Stannic phosphate membranes.

$$E_m = -\frac{RT}{F}\left[\ln\frac{C_2}{C_1} + (2\alpha-1)\ln\frac{(4C_2^2+\beta^2X^2)^{\frac{1}{2}}+(2\alpha-1)\beta X}{(4C_1^2+\beta^2X^2)^{\frac{1}{2}}+(2\alpha-1)\beta X} - \ln\frac{(4C_2^2+\beta^2X^2)^{\frac{1}{2}}+\beta X}{(4C_1^2+\beta^2X^2)^{\frac{1}{2}}+\beta X}\right] \qquad (2.10)$$

where β is a characteristic factor of the membrane - electrolyte pair, and represents the fraction of counterions not tightly bound to membrane skeleton. The product βX is termed the thermodynamically effective fixed charge density of a membrane; the other terms have their usual significance. Equation 2.10 reduced to the TMS membrane potential equation (eq. 2.2) for $\beta=1$. Since it was sometimes troublesome to evaluate βX at an arbitrary external electrolyte concentration from the observed membrane potential using this equation Kobatake and Kano (13) have proposed a simple method using the following approximate equation for the diffusive contribution to the emf of cell with transport :

$$E_m = -\frac{RT}{F}(1-2\,t_{-,pp})\ln(C_2/C_1) \qquad (2.11)$$

where $t_{-,pp}$ is the apparent transference number of anions in the membrane phase. Comparison of equations 2.10 and 2.11 gives

$$t_{+,m} = \frac{1+\alpha}{2} \frac{\ln\left(\dfrac{\sqrt{4\xi_2^2+1}+2\alpha-1}{\sqrt{4\xi_1^2+1}+2\alpha-1}\right)}{\ln\gamma} + \frac{\ln\left(\dfrac{\sqrt{4\xi_2^2+1}+1}{\sqrt{4\xi_1^2+1}+1}\right)}{2\ln\gamma} \qquad (2.12)$$

where $\xi_i = C / \beta x$

On the other hand (12.13), the mean fixed transference number of cations in a negatively charged membrane immersed in an electrolyte solution of concentration C was defined by

$$t_- = \nu\bar{C}_- / (u\bar{C}_+ + \nu\bar{C}_-) \qquad (2.13)$$

where $\bar{C}_+$ and $\bar{C}_-$ are the concentrations of cations and anions, respectively in the membrane phase. This equation was transformed to

$$t_- = 1 - \alpha \frac{\sqrt{4\xi_2^2+1}+1}{\sqrt{4\xi_1^2+1}+(2\alpha-1)} \qquad (2.14)$$

using certain equations for the activity coefficients, mobilities of small ions in the membrane phase, and the equilibrium condition for electrical neutrality (12.13).

The difference between the apparent transference number t_{-app} calculated from eq. 2.12 and t_- from equation 2.14 for various reduced concentrations ξ ($\xi = C / \bar{X}$) was found to be always less than 2% over a wide range of external electrolyte concentrations. Therefore, t_{-app} and t_- were considered practically the same. As a result, the apparent transference number evaluated from the membrane potential data was used for the determination of the thermodynamically effective fixed charge density $\bar{X}$ of the membrane at a given average salt concentration C [C = $(C_1 + C_2) / 2$] using equation 2.14 and provides a definition of permselectivity P_e by the expression

$$\frac{1}{(4\xi^2 + 1)^{\frac{1}{2}}} = \frac{1 - t_- - \alpha}{\alpha - (2\alpha - 1)(1 - t_-)} \equiv P_e \qquad (2.15)$$

This equation can be used to find the permselectivity from membrane potential measurements using equation 2.11. If the transport number of cations (t_- or t_{-app}) is unity, the membrane is perfectly selective and $P_e = 1$, while if the transport number of anions has the free solution value $P_e = 0$. The values of P_e (Tables 2.11-2.18) obtained using the right hand side of equation 2.15 were plotted against log C. The concentration at which P_e (where $\xi = C / \bar{X} = 1$) becomes equal to $(1/2)^{\frac{1}{2}}$

TABLE 2.11

VALUES OF PERMSELECTIVITY P_e OF THE MEMBRANE USING VARIOUS 1:1 ELECTROLYTES AT DIFFERENT CONCENTRATIONS FOR STANNOUS FERROCYANIDE MEMBRANE

Electrolyte Concentration C_2/C_1 (mol/ℓ)	KCl	NaCl	LiCl
$1 / 1 \times 10^{-1}$	0.10	0.04	0.12
$5 \times 10^{-1} / 5 \times 10^{-2}$	0.14	0.10	0.20
$1 \times 10^{-1} / 1 \times 10^{-2}$	0.31	0.30	0.30
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.37	0.46	0.40
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.57	0.56	0.50
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.78	0.67	0.69
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.82	0.76	0.70

Vide Fig. 2.8(a)

TABLE 2.12

VALUES OF PERMSELECTIVITY P_e OF THE MEMBRANE USING VARIOUS 1:1 ELECTROLYTES AT DIFFERENT CONCENTRATIONS FOR STANNIC FERROCYANIDE MEMBRANE

Electrolyte Concentration C_2/C_1 (mol/ℓ)	KCl	NaCl	LiCl
$1 / 1 \times 10^{-1}$	0.02	0.04	0.06
$5 \times 10^{-1} / 5 \times 10^{-2}$	0.14	0.12	0.16
$1 \times 10^{-1} / 1 \times 10^{-1}$	0.27	0.20	0.26
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.37	0.30	0.44
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.72	0.60	0.62
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.87	0.82	0.78
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.90	0.87	0.82

Vide Fig. 2.8(b)

TABLE 2.13

VALUES OF PERMSELECTIVITY P_a OF THE MEMBRANE USING VARIOUS 1:1 ELECTROLYTES AT DIFFERENT CONCENTRATIONS FOR STTANIC PHOSPHATE MEMBRANE

Electrolyte Concentration C_2/C_1 (Mol/ℓ)	KCl	NaCl	LiCl
$1 / 1 \times 10^{-1}$	0.04	0.11	0.22
$5 \times 10^{-1} / 5 \times 10^{-2}$	0.08	0.13	0.25
$1 \times 10^{-1} / 1 \times 10^{-2}$	0.15	0.22	0.29
$5 \times 10^{-2} / 5 \times 10^{-3}$	0.32	0.39	0.40
$1 \times 10^{-2} / 1 \times 10^{-3}$	0.52	0.53	0.46
$5 \times 10^{-3} / 5 \times 10^{-4}$	0.63	0.60	0.56
$1 \times 10^{-3} / 1 \times 10^{-4}$	0.70	0.65	0.61

Vide Fig. 2.8(a)

gives the value of thermodynamically effective fixed charge density $\bar{X}$ as required by left side of equation 2.15. Fig. 2.8 (a, b and c) represent plots of P_s versus log $(C_1 + C_2) / 2$ for polystyrene bonded stannous ferrocyanide, stannic ferrocyanide and stannic phosphate membranes in contact with various 1:1 electrolytes. The value of $\bar{X}$ thus derived for the membranes and 1:1 electrolyte combinations are given in Table 2.14.

Tasaka et al. (17) derived another equation for the membrane potential existing across a charged membrane. The total membrane potential E_m was considered as the sum of a diffusion potential E_d inside the membrane and the electrostatic potential difference E_e between the membrane surfaces and the electrolyte solutions on both sides of the membrane. The diffusion potential E_d was obtained by integrating the basic flow equation for diffusion while the electrostatic potential difference was calculated from the Donnan theory, stated mathematically,

$$E_m = E_d + E_e \qquad (2.16)$$

where

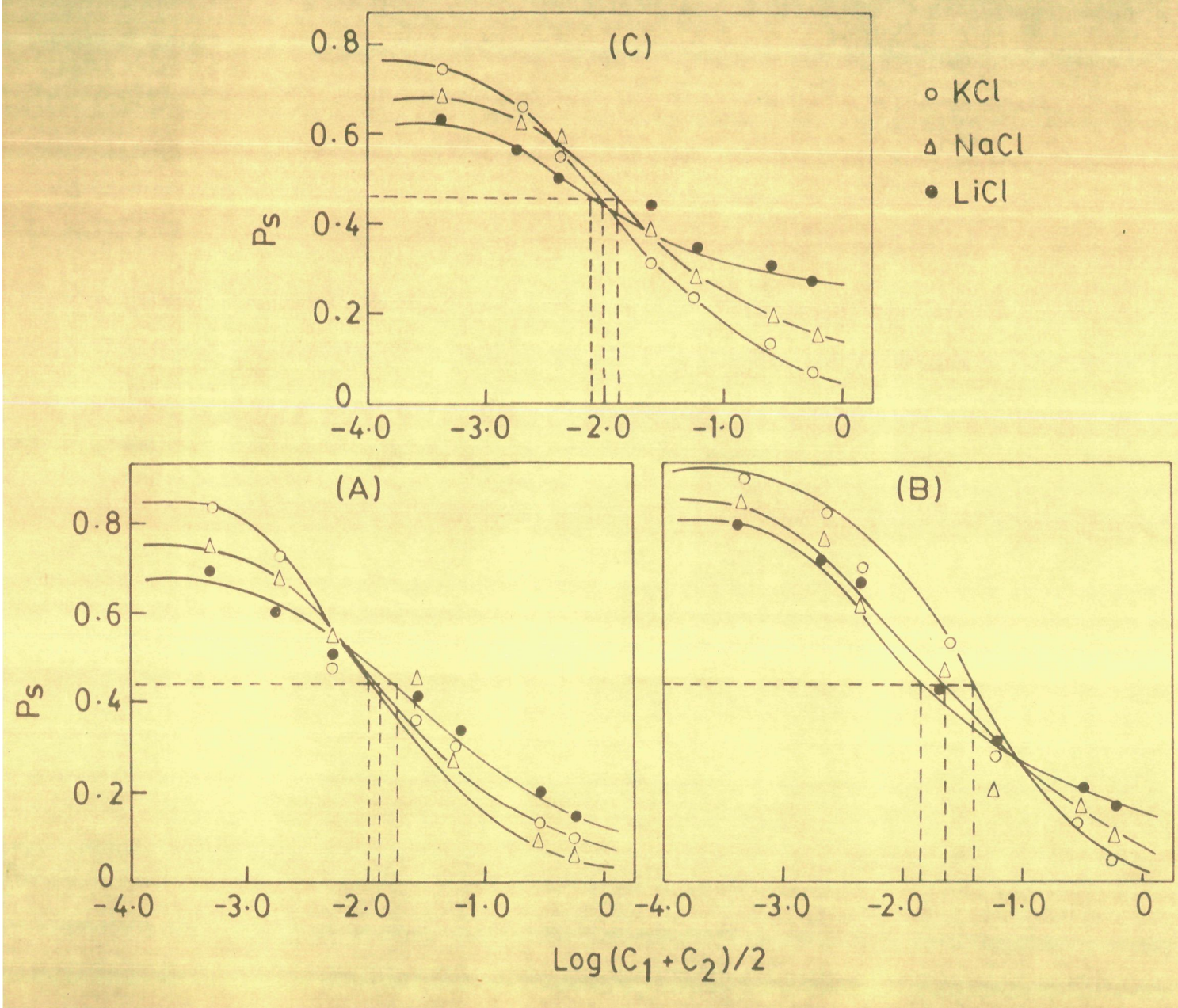


Fig.2·8: Plots of Ps against $\log(C_1+C_2)/2$ for (A) Stannous ferrocyanide, (B) Stannic ferrocyanide and (C) Stannic phosphate membranes.

TABLE 2.14

VALUES OF EFFECTIVE FIXED CHARGE DENSITY ϕX(eq/l) OBTAINED FROM KOBATAKE'S PERMSELECTIVITY METHOD FOR VARIOUS MEMBRANE ELECTROLYTE SYSTEMS AT 25±0.1°C

Electrolyte Membranes	KCl	CaCl	LiCl
Stannous Ferrocyanide			
$(\phi X) \times 10^3$, eq/l	7.1	5.9	5.2
Stannic Ferrocyanide			
$(\phi X) \times 10^3$, eq/l	8.0	7.2	6.0
Stannic Phosphate			
$(\phi X) \times 10^3$, eq/l	8.4	7.8	5.8

$$-\varepsilon_d = -\int_1^2 \frac{J_0}{F\bar{c}_0} \frac{\beta X}{(\bar{z}_- + \beta x)u + \bar{z}_- v} dx +$$

$$\frac{RT}{F}\int_1^2 \frac{(\bar{z}_- + \beta x)u}{(\bar{z}_- + \beta x)u + \bar{z}_- v} d\ln\bar{c}_+ -$$

$$\frac{RT}{F}\int_1^2 \frac{\bar{z}_- v}{(\bar{z}_- + \beta x)u + \bar{z}v} d\ln\bar{c}_- \qquad (2.17)$$

where a_1 and a_2 are the activities of the electrolytes on the two sides of the membrane, bars indicate the membrane phase, J_0 is the flux of electrolyte in the absence of an external electric field and other symbols have their usual significance. Integrating eq 2.17 in the limit of high electrolyte concentrations across the membrane, one obtains the following equation for the membrane potential:

$$-\varepsilon_m = \frac{RT}{F}\left(\frac{\beta X}{2}\right)\left(\frac{\gamma-1}{\gamma}\right)\frac{1}{\bar{c}_2} + \frac{RT}{F}\left(\frac{u-v}{uv}\right)\left[\frac{1-\frac{\beta X}{RT\bar{c}_0(u-v)X}}{1-\frac{\beta X}{2RT\bar{c}_0 vX}}\right]\ln\gamma$$

$$+\frac{RT\beta X}{2Fuv}\left(\frac{J_0}{RT\bar{c}_0 X}\right)^2 \frac{\left[1-\frac{\beta X}{4RT\bar{c}_0 uvX}\right]}{\left[1-\frac{\beta X}{2RT\bar{c}_0 vX}\right]^2}(\gamma-1)c_1 \qquad (2.18)$$

TABLE 2.15

VALUES OF EFFECTIVE FIXED CHARGE DENSITY $\bar{f}X$(eq/ℓ) OBTAINED FROM TASAKA'S METHOD FOR VARIOUS MEMBRANE ELECTROLYTE SYSTEMS AT 25 ± 0.1°C

Electrolyte Membranes	KCl	NaCl	LiCl
Stannous Ferrocyanide			
$(\bar{f}X) \times 10^3$, eq/ℓ	7.0	5.5	4.0
Stannic Ferrocyanide			
$(\bar{f}X) \times 10^3$, eq/ℓ	7.7	6.8	6.0
Stannic Phosphate			
$(\bar{f}X) \times 10^3$, eq/ℓ	8.8	7.0	6.0

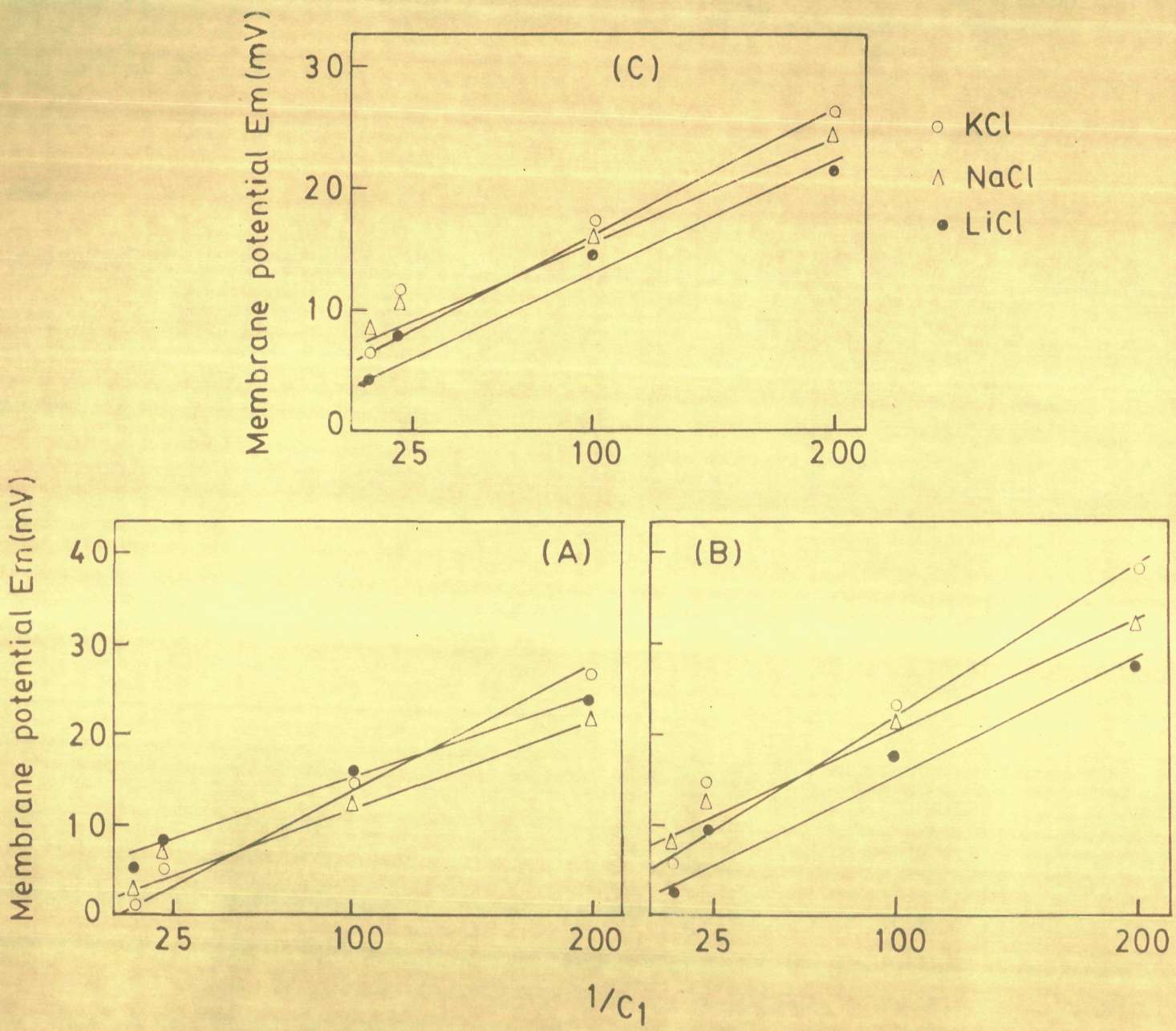


Fig. 2·9: Plots of membrane potential Em (mV) against $^{1}/_{C_1}$ for (A) Stannous ferrocyanide, (B) Stannic ferrocyanide and (C) Stannic phosphate membranes.

At high electrolyte concentration, eq. 2.18 can be approximated to

$$-E_m = \frac{RT}{F} \left(\frac{\gamma \pm i}{\gamma}\right) \left(-\frac{F\bar{X}}{2}\right) \frac{1}{C_1} \quad \text{(2.19)}$$

Eq. 2.19 predicts a linear relationship between E_m and $1/C_1$ from which $\bar{X}$ can be calculated. Plots of E_m Vs. $1/C_1$ (Fig. 2.9 a, b and c) are in agreement with eq.2.19 The values of $\bar{X}$ derived from the slope of lines are given in Table 2.18

It is noted from Table 2.5, 2.12, 2.14 and 2.15 that the values of the effective fixed charge densities evaluated from the different methods are almost the same. The slight deviations may be accounted to the different procedure adopted for the evaluation. It may, therefore, be concluded that the methods developed recently for the evaluation of effective fixed charge density are valid for the membranes under investigation.

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Bionic Potential, Electrical Conductivity and Generic Membrane Theories

When a membrane is used to separate solutions of two electrolytes with common anion or cation (AP_1 BP or AX_1 AY type) at the same concentration, the steady potential developed is called bionic potential (BIP) (1) which is a measure of the selectivity of the membrane for ions of the same sign. BIP has been considered by Helfferich (2) in accordance with the concepts of TMS theory (3,4), as being the algebraic sum of two interfacial potentials and an internal diffusion potential.

For biological membranes this potential difference is usually described in terms of the Goldman-Hodgkin-Katz equation (5,6)

$$E = \frac{RT}{F} \ln \frac{a_K' + \frac{P_{Na}}{P_K} a_{Na}' + \frac{P_{Cl}}{P_K} a_{Cl}}{a_K'' + \frac{P_{Na}}{P_K} a_{Na}'' + \frac{P_{Cl}}{P_K} a_{Cl}''} \qquad (3.1)$$

P_{Na} / P_K and P_{Cl} / P_K represent a set of coefficients defined from measurements under various external solution conditions. Whereas for certain ion exchange membranes permeable mainly to cations of one sign (e.g.

actions) E is described by a generalized Nernst equation.

$$E = \frac{RT}{F} \ln \frac{\sum_i a_i P_i^+}{\sum_j a_j P_j^+} \qquad (3.2)$$

Derivation of equations for bionic potential have been made from various theoretical considerations: Hodgkin and Katz (6), following Goldman (5), derived eq. 3.1 for the steady state with constant permeability ratios assuming a constant electric field to exist within the membrane. An equation for E valid also in non steady state was derived by Henderson (7) assuming a mixture boundary. In the case of equal total concentrations and the common anion, the Henderson equation becomes identical in form to eq. 3.1. When the total concentrations on either side of the membrane are equal, eq. 3.1 is also derived from Teorell's fixed charge theory for membranes with a uniform site distribution (8).

On the other hand, eq. 3.2 has been derived by Conti and Eisenman (9) without assuming a constant field for ion exchange membranes, permeable solely to ions of one sign and having macroscopically distributed fixed sites of constant chemical properties.

Equation 3.2 has also been shown to describe the

potential of a completely dissociated liquid ion exchange membrane, although only in the steady state (10). Due to the wide variety of systems to which eqs. 3.1 and 3.2 appear to apply and because equations of a similar form can be deduced from such diverse initial assumptions, Sandblom and Eisenman (11) speculated the possibility and derived a general expression for E with the permeability ratios treated as phenomenological coefficients without specifying the permeation mechanism. Such equations have also been accomplished for the steady state case by Patlak (12) and by Kimizuka (13).

In recent years several other equations for bionic potential applicable to membrane-electrolyte systems based on the thermodynamics of irreversible processes, which does not require any prior knowledge of the concentration profiles or the permeation mechanism, have been derived and their validity examined.

In this chapter, the bionic potentials observed across permanent supported silver, manganese and cobalt ferrocyanide membranes separating 1:1 electrolyte solution with common cations, and the conductivity of the membranes in contact with different concentrations of 1:1 electrolytes have been described for the evaluation of the selectivity character of the membranes using the equation relating permeability ratio and mobility ratio.

EXPERIMENTAL PROCEDURE

The ionic potentials across freshly prepared silver ferrocyanide, manganese ferrocyanide and cobalt ferrocyanide membranes were measured by constructing an electrochemical cell of the following type, and using a pye-precision vernier potentiometer.

SCE	Electrolyte Solution ix (/)	Membrane	Electrolyte Solution jx (//)	SCE

For the measurement of electrical conductivity, membranes were first dipped and equilibrated in an appropriate electrolyte solution. It was then clamped between two half cells and measurements were made (as shown in chapter 1(Fig.1.1) using a conductivity bridge (Cambridge Instrument Co., Ltd., England). The error in the measurements of membrane potential was within ± 1% whereas electrical conductivity could be measured to better than 99.5%.

RESULTS AND DISCUSSION

When an ion exchange membrane is interposed between two solutions of the same electrolyte, but of different concentrations, the potential difference developed is called the concentration potential or membrane potential. The sign and magnitude of this emf gives the selectivity of the membrane towards the ions of the electrolyte. But if the membrane is used to separate solution of the two electrolytes of the type ix and jx (or ix and iy), the steady potential developed is called bionic potential (BIP) (1) which is a measure of the selectivity of the membrane for ions of the same sign. BIP has been considered by Helfferich (2) in accordance with the concepts of the TMS theory (3,4), as being the algebraic sum of two interfacial potentials and an internal diffusion potential. A complete mathematical discussion under conditions: (a) membrane diffusion control, (b) film diffusion control and (c) coupled membrane film diffusion control has been presented (2). For a general case involving complete membrane diffusion control, the BIP for concentrations is given by

$$E = \frac{RT}{F} \ln\left[\frac{u_i q_i \bar{v}_j x_j}{u_j q_j \bar{v}_i x_j}\right] = \frac{RT}{F} \ln\left[\frac{x_{jx}(u_i q_i \bar{v}_j)}{u_j q_j \bar{v}_i}\right] \quad \ldots(3.3)$$

where $a_i / a_j = \bar{U}_i / \bar{U}_j = \bar{V}_i / \bar{V}_j$ are the ratio of the activities, diffusion coefficients, and the conductivity coefficients of the counterions i and j respectively. Overbars refer the phenomena in the membrane phase, R, T, Z and F have their usual meanings. Using the Einstein's relation $D_i = U_i RT$ and the generalized Nernst equation in which the permeability ratios are independent of external electrolyte solutions, equation 3.3 reduces to the form

$$E = \frac{RT}{ZF} \ln \left[\frac{a_i \bar{U}_i}{a_j \bar{U}_j} K_{ji} \right] = \frac{RT}{ZF} \ln \left[\frac{a_i \bar{P}_i}{a_j \bar{P}_j} \right] \qquad (3.4)$$

equation 3.4 gives

$$\bar{P}_i / \bar{P}_j = K_{ji} \frac{\bar{U}_i}{\bar{U}_j} \qquad (3.5)$$

This equation has also been derived most recently by Sandblom and Eisenman (11) from thermodynamic treatment for fixed site membrane which implies that the permeability ratio is, quite generally, related to the ion exchange equilibrium constant K_{ij} and the ratio of mobilities of the optional ions. Further, using the well known relation

$$\bar{U}_i / \bar{U}_j = \bar{\lambda}_i / \bar{\lambda}_j$$

equation 3.8 gives

$$\bar{P}_i / \bar{P}_j = K_{ji} \frac{\bar{U}_i}{\bar{U}_j} = K_{ji} \frac{\bar{\lambda}_i}{\bar{\lambda}_j} \qquad (3.8)$$

where $\bar{\lambda}_i$ is the conductivity of the membrane when it is wholly in i form and $\bar{\lambda}_j$ is the conductivity of the membrane when it is wholly in the j form.

Dilonic potential measurements were carried out by interposing the membrane between two different electrolyte solutions at the same concentration. The DIP values were low when the membranes were used to separate concentrated electrolyte solutions whereas it increased with decreasing salt concentrations(Tables 3.1 - 3.3) and depicted in Fig. 3.1 (a, b and c) against log C. The permeability ratio $\bar{P}_i / \bar{P}_j$ calculated from these DIP values using eq. 3.4 were seen to be concentration dependent (Tables 3.4 - 3.6). This behaviour was seen with all the three membranes and different electrolyte pairs. The variation in DIP caused by the changes produced in the permeability ratio may be ascribed due to structural changes produced at the membrane-solution interfaces. Parchment supported inorganic precipitate membranes contain exchangeable groups as part of its structure which may account for its negative charge.

TABLE 3.1

EXPERIMENTAL VALUES OF DIFFUSION POTENTIAL E_{DP}(mV) ACROSS SILVER FERROCYANIDE MEMBRANE AT 28 ± 0.1°C

Electrolyte Concentration(Mol/l)	KCl-NaCl	KCl-LiCl	NaCl-LiCl
1×10^{-1} / 1×10^{-1}	7.4	1.6	3.2
5×10^{-2} / 5×10^{-2}	8.9	3.5	5.4
2×10^{-2} / 2×10^{-2}	10.8	4.8	6.1
1×10^{-2} / 1×10^{-2}	14.5	7.4	19.0
5×10^{-3} / 5×10^{-3}	15.0	8.4	20.0
2×10^{-3} / 2×10^{-3}	15.8	10.4	21.5
1×10^{-3} / 1×10^{-3}	16.3	11.7	22.0

Vide Fig. 3.1(a)

TABLE 3.2

EXPERIMENTAL VALUES OF DIFFUSION POTENTIAL E_{DP}(mV) ACROSS MANGANESE FERROCYANIDE MEMBRANE AT 28 ± 0.1°C

Electrolyte Concentration(Mol/l)	KCl-NaCl	KCl-LiCl	NaCl-LiCl
1×10^{-1} / 1×10^{-1}	2.3	4.6	1.8
5×10^{-2} / 5×10^{-2}	4.8	6.8	3.2
2×10^{-2} / 2×10^{-2}	6.3	7.4	5.0
1×10^{-2} / 1×10^{-2}	8.6	13.0	16.0
5×10^{-3} / 5×10^{-3}	11.6	14.8	19.0
2×10^{-3} / 2×10^{-3}	18.1	11.9	22.8
1×10^{-3} / 1×10^{-3}	18.8	21.0	25.0

Vide Fig. 3.1(b)

TABLE 3.3

EXPERIMENTAL VALUES OF DIIONIC POTENTIAL E_{DIP}(mV) ACROSS COBALT FERROCYANIDE MEMBRANE AT 25 ± 0.1°C

Electrolyte Concentration(Mol/l)	KCl-NaCl	KCl-LiCl	NaCl-LiCl
1×10^{-1} / 1×10^{-1}	6.5	0.4	5.6
5×10^{-2} / 5×10^{-2}	7.2	1.5	7.5
2×10^{-2} / 2×10^{-2}	8.5	2.0	10.1
1×10^{-2} / 1×10^{-2}	10.4	6.5	15.5
5×10^{-3} / 5×10^{-3}	11.5	7.2	17.6
2×10^{-3} / 2×10^{-3}	12.2	8.3	21.6
1×10^{-3} / 1×10^{-3}	18.4	10.0	23.5

Vide Fig. 3.1(a)

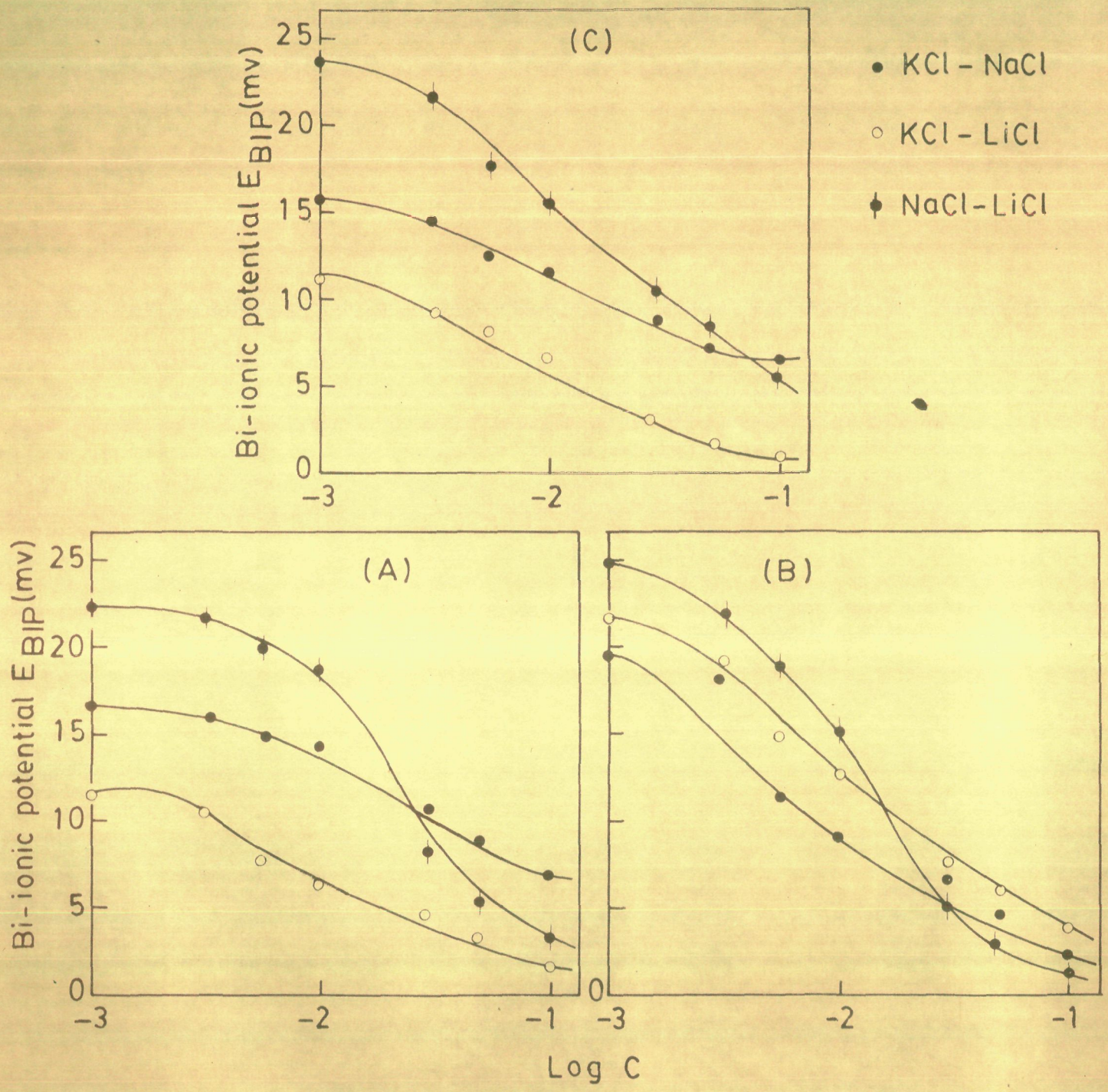

Fig. 3·1: Plots of bi-ionic potential E(mV) against log C for (A) Silver ferrocyanide, (B) Manganese ferrocyanide and (C) Cobalt ferrocyanide membranes using 1:1 Electrolyte pairs.

TABLE 3.4

VALUES OF THE INTRAMEMBRANE PERMEABILITY RATIO OF VARIOUS 1:1 ELECTROLYTE ION PAIRS ACROSS SILVER FERROCYANIDE MEMBRANE

Electrolyte(ion pair) Concentration(Mol/l)	P_{K^+}/P_{Na^+}	P_{K^+}/P_{Li^+}	P_{Na^+}/P_{Li^+}
1×10^{-1} / 1×10^{-1}	1.3	1.1	1.1
5×10^{-2} / 5×10^{-2}	1.4	1.2	1.2
2×10^{-2} / 2×10^{-2}	1.5	1.2	1.3
1×10^{-2} / 1×10^{-2}	1.7	1.3	1.9
5×10^{-3} / 5×10^{-3}	1.8	1.4	2.1
2×10^{-3} / 2×10^{-3}	1.8	1.5	2.3
1×10^{-3} / 1×10^{-3}	1.9	1.6	2.3

TABLE 3.5

VALUES OF THE INTRAMEMBRANE PERMEABILITY RATIO OF VARIOUS 1:1 ELECTROLYTE ION PAIRS ACROSS MANGANESE FERROCYANIDE MEMBRANE

Electrolyte(ion pair) Concentration(Mol/l)	P_{K^+}/P_{Na^+}	P_{K^+}/P_{Li^+}	P_{Na^+}/P_{Li^+}
1×10^{-1} / 1×10^{-1}	1.1	0.9	0.8
5×10^{-2} / 5×10^{-2}	1.2	0.9	0.9
2×10^{-2} / 2×10^{-2}	1.3	1.0	1.1
1×10^{-2} / 1×10^{-2}	1.4	1.1	1.1
5×10^{-3} / 5×10^{-3}	1.6	1.1	1.2
2×10^{-3} / 2×10^{-3}	2.1	1.5	1.4
1×10^{-3} / 1×10^{-3}	2.2	1.6	1.7

TABLE 3.6

VALUES OF THE INTRAMEMBRANE PERMEABILITY RATIO OF VARIOUS 1:1 ELECTROLYTE ION PAIRS ACROSS COBALT FERROCYANIDE MEMBRANE

Electrolyte(ion pair) Concentration(mol/l)	P_{K^+}/P_{Na^+}	P_{K^+}/P_{Li^+}	P_{Na^+}/P_{Li^+}
1×10^{-1} / 1×10^{-1}	1.2	1.0	1.1
5×10^{-2} / 5×10^{-2}	1.2	1.0	1.2
2×10^{-2} / 2×10^{-2}	1.4	1.1	1.3
1×10^{-2} / 1×10^{-2}	1.7	1.2	1.5
5×10^{-3} / 5×10^{-3}	2.0	1.3	1.9
2×10^{-3} / 2×10^{-3}	2.1	1.4	2.2
1×10^{-3} / 1×10^{-3}	2.3	1.5	2.4

The exchangeable cations will be free to move in the pores. Within the pores there will be a diffused ionic atmosphere from the charged wall. Since the membranes under investigation carry low site densities (charge density 1 x 10^{-3} eq/l), anion enchroachment into the membrane seems to be the most probable phenomena. The thickness of the atmosphere depends upon the electrolyte concentration. In very dilute solutions of electrolyte, the thickness becomes so great that only cations are present in the pores and the membrane becomes impermeable to anions, a condition necessary for the derivation of eq. 3.4 with constant permeability ratio. Thus the best data on $\bar{P}_i / \bar{P}_j$ is that from the most dilute solutions. It may, therefore, be concluded that the existence of an expression for E with constant permeability ratios cannot be characteristic of all the membranes but is restricted to certain physical situations, most notably those in which a membrane is permeable only to species of one sign. This is in agreement with the mathematical treatment advanced by Sandblom and Kleemann (41).

In order to have a knowledge of selectivity K_{ij} from the predetermined values of $\bar{P}_i / \bar{P}_j$, the ratio of electrical conductivities $\bar{\lambda}_i / \bar{\lambda}_j$ as demanded

TABLE 3.7

EXPERIMENTAL VALUES OF MEMBRANE ELECTRICAL CONDUCTANCE (MHOS) ACROSS SILVER FERROCYANIDE MEMBRANE FOR EQUIVALENT ELECTROLYTES AT 25 ± 0.1°C

Electrolyte Concentration(Mol/l)	KCl	NaCl	LiCl
1×10^{-1} / 1×10^{-1}	0.44×10^{-1}	0.38×10^{-1}	0.33×10^{-1}
5×10^{-2} / 5×10^{-2}	0.40×10^{-1}	0.30×10^{-1}	0.28×10^{-1}
2×10^{-2} / 2×10^{-2}	1.50×10^{-2}	1.30×10^{-2}	0.99×10^{-2}
1×10^{-2} / 1×10^{-2}	1.19×10^{-2}	0.88×10^{-2}	0.69×10^{-2}
5×10^{-3} / 5×10^{-3}	0.68×10^{-2}	0.48×10^{-2}	0.38×10^{-2}
2×10^{-3} / 2×10^{-3}	0.50×10^{-2}	0.43×10^{-2}	0.40×10^{-2}
1×10^{-3} / 1×10^{-3}	2.50×10^{-3}	2.90×10^{-3}	2.30×10^{-3}

Vide Fig. 3.2(a)

TABLE 3.8

EXPERIMENTAL VALUES OF MEMBRANE ELECTRICAL CONDUCTANCE $\times 10^{3}$(MHOS) ACROSS MANGANESE FERROCYANIDE MEMBRANE AT 25 ± 0.1 °C

Electrolyte Concentration(Mol/l)	KCl	NaCl	LiCl
1×10^{-1} / 1×10^{-1}	0.56	0.47	0.43
5×10^{-2} / 5×10^{-2}	0.77	0.62	0.54
2×10^{-2} / 2×10^{-2}	1.28	1.02	0.86
1×10^{-2} / 1×10^{-2}	2.12	1.63	1.39
5×10^{-3} / 5×10^{-3}	3.90	2.80	2.48
2×10^{-3} / 2×10^{-3}	5.00	3.12	2.86
1×10^{-3} / 1×10^{-3}	5.70	3.25	2.83

Vide Fig. 3.2(b)

TABLE 3.2

EXPERIMENTAL VALUES OF MEMBRANE ELECTRICAL CONDUCTANCE (MHOS) ACROSS COBALT FERROCYANIDE MEMBRANE FOR MONOVALENT ELECTROLYTES AT 28 ± 0.1 °C

Electrolyte Concentration(mol/ℓ)	KCl	NaCl	LiCl
1×10^{-1} / 1×10^{-1}	0.80×10^{-2}	0.77×10^{-2}	0.67×10^{-2}
5×10^{-2} / 5×10^{-2}	0.64×10^{-2}	0.48×10^{-2}	0.40×10^{-2}
2×10^{-2} / 2×10^{-2}	0.34×10^{-2}	0.25×10^{-2}	0.20×10^{-2}
1×10^{-2} / 1×10^{-2}	2.30×10^{-3}	1.80×10^{-3}	1.50×10^{-3}
5×10^{-3} / 5×10^{-3}	2.30×10^{-3}	1.38×10^{-3}	1.30×10^{-3}
2×10^{-3} / 2×10^{-3}	1.60×10^{-3}	0.90×10^{-3}	0.85×10^{-3}
1×10^{-3} / 1×10^{-3}	1.10×10^{-3}	0.60×10^{-3}	0.50×10^{-3}

Vide Fig. 3.2(a)

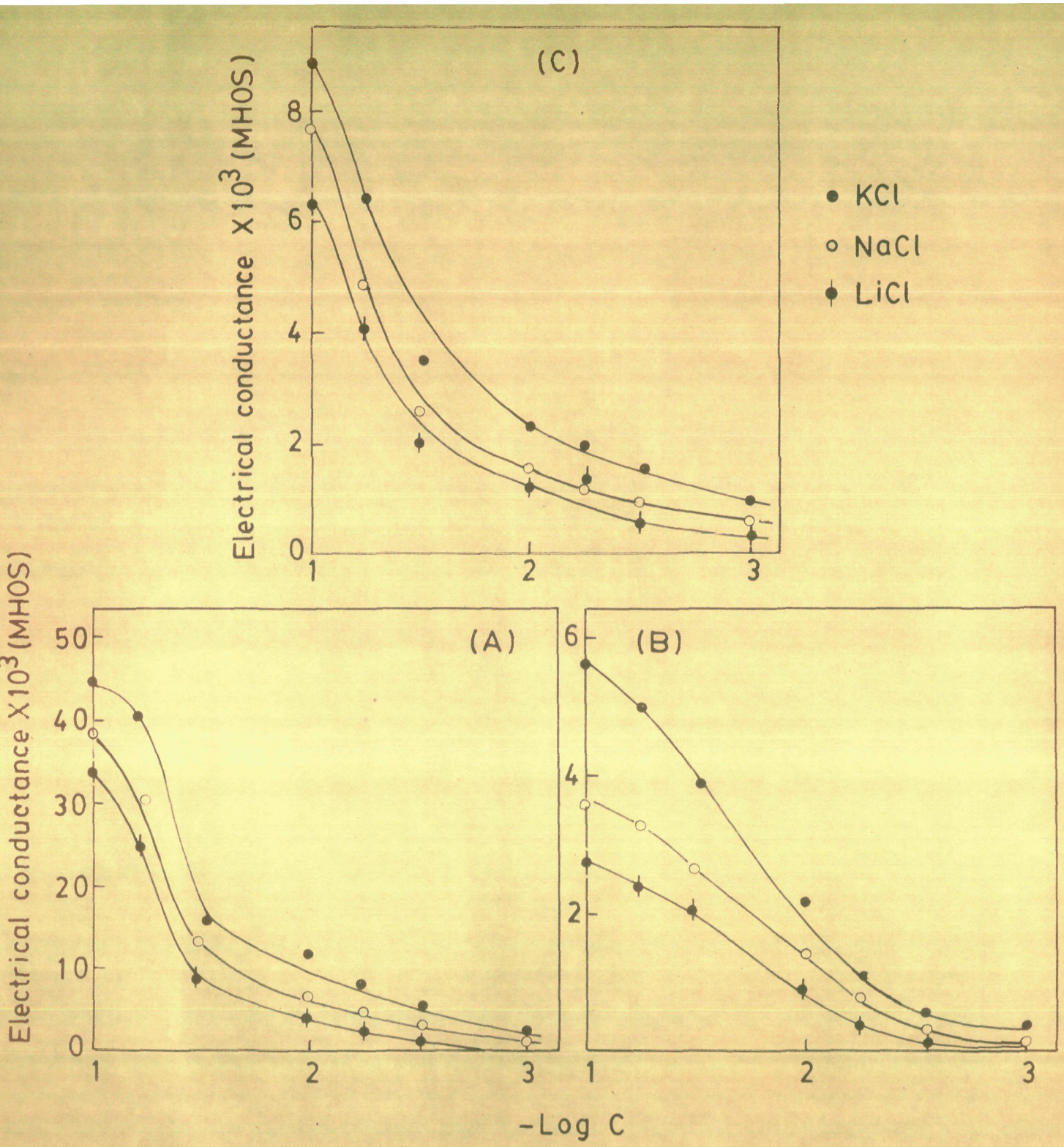

Fig. 3·2: Plots of electrical conductance (MHOS) against -log C for (A) Silver ferrocyanide, (B) Manganese ferrocyanide and (C) Cobalt ferrocyanide membranese.

TABLE 3.10

VALUES OF SELECTIVITY CONSTANT (K_{ij} Pot) FOR VARIOUS MEMBRANES CALCULATED FROM DIFFUSION POTENTIALS E_{Dif}(mV) AND CONDUCTANCE (MHOS)

Selectivity Constant Membranes	K_{K-Na}	K_{K-Li}	K_{Na-Li}
Silver Ferrocyanide	1.10	1.11	1.19
Manganese Ferrocyanide	1.12	1.15	1.20
Cobalt Ferrocyanide	1.18	1.10	1.13

by eq. 3.6 must be known. Membrane conductance measurements were carried out when it was wholly in the form i or wholly in the form j. The values of membrane conductance at various electrolyte concentration are given in Tables 3.7 - 3.9. The values are relatively more dependent upon the concentration of the electrolyte within the membrane as shown in fig. 3.2 (a, b and c). This implies that the membranes have a relatively high Donnan uptake of anion and a low selectivity constant value. This is in agreement with the findings of Heymann and Robinov (14), Spiegler et al (15) and our findings with ion exchange membranes (16-23). The value of selectivity K_{ij} evaluated from the ratio of electrical conductivities $\bar{\lambda}i / \bar{\lambda}j$ and the intra-membrane permeability ratio $\bar{P}_i / \bar{P}_j$ using eq. 3.6 are given in Tables 3.4 - 3.6. The values of K_{ij} point towards the fact that the selectivity of the membranes increases with the decrease in concentration of the external electrolyte solutions and that the selectivity sequence of the membranes for the cations was as follows

$$K > Na > Li$$

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ABSTRACT

Transport processes occurring across parchment supported and polystyrene based inorganic precipitate membranes have been investigated by taking into the ionic transport, membrane potential, electrical conductivity, ionic distribution equilibria, and spatial distribution of ions and potential within the membrane.

The work described in the thesis has been divided into three parts.

Part I deals with the conductance measurements of parchment supported silver ferrocyanide, manganese ferrocyanide and cobalt ferrocyanide membranes in contact with different concentrations of a number of electrolytes at 10, 15, 20, 25, 30 and 35 ($\pm 0.1^{\circ}C$). The conductance data have been used to calculate various thermodynamic parameters like Energy of activation E_a, Free energy of activation $\Delta F^{\#}$, and Entropy of activation $\Delta S^{\#}$ etc. by the application of absolute reaction rate theory. The results of the investigations are that the membrane conductance can be determined at different temperatures with reasonable accuracy. The membranes are weakly charged and ionic species retain

their hydration shell, at least partially, while diffusing through the membrane pores. Negative $\Delta S^{\ddagger}$ values suggest that the partial immobilization of ion takes place. The immobility of ions within the membrane phase has been ascribed to the interstitial permeation, and the interactions of ions with the fixed charge groups of the membrane skeleton. The interionic distance (or jump distance) for the systems under investigation have been found to be 1.5 A^{0} which is consistent with the empirical values chosen by various investigators.

Part II deals with the characterization and evaluation of effective fixed charge density of polystyrene based stannous ferrocyanide, stannic ferrocyanide, and stannic phosphate membranes in contact with various 1:1 electrolytes at different concentrations from the membrane potential measurements. The Teorell-Meyer and Sievers method; the methods developed by Kobatake and [illegible] and the most recently developed method of Tanaka et al, based on the principles of irreversible thermodynamics were utilized for the charge density determinations.

The values of effective fixed charge densities evaluated from the different methods were almost the same. The slight deviations has been accounted to the

different procedure adopted for the evaluation. Various theoretical predictions of the Kobatake et. al's theory as well as those of Tasaka et. al's theory were borne out quite satisfactorily by our experimental results. It has, therefore, been concluded that the methods developed recently based on thermodynamics of irreversible processes for the evaluation of effective fixed charge density are valid for the membrane-electrolyte systems under investigation and other such systems.

Part III of the thesis describes the evaluation of selectivity of the parchment supported inorganic precipitate membranes towards simple metal ions from bionic potential and electrical conductance measurements. The selectivity sequence of membranes for cations were as follows:

$$K^{+} > Na^{+} > Li^{+}$$